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A NON-SILVER BASED PHOTOGRAPHIC PROCESS

and

THE CRYSTAL AND MOLECULAR STRUCTURE OF

3,7-Dihydroxy-1,5-Bis(p-Bromophenyl) Octahydro-1,5-Diazocine

by

CARY Y. PETERS

A thesis Submitted in Partial
Fulfillment of the Requirements for the Degree
Master of Science, Major in Chemistry,
South Dakota State University

1975

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This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Major Advisor/

Date

Head, Chemistry Department

Date

ACKNOWLEDGEMENTS

I would like to thank James J. Worman and Roy Odle for preparation of the compound used in this study. Thanks also to Charles Matthews and Del Johnson for their help in the many computer programming difficulties.

A special thank you to William Jensen who was my advisor for both projects. His friendship, guidance and the fact that he was never too busy to help during the many trying times will not be forgotten.

To Donna Dobbs, who helped me piece my thesis together, thanks a million.

To the faculty and the many friends I've come to know while at South Dakota State University, thank you for the learning and growing experience of the last two years.

To my family for their constant encouragement, concern and love throughout my education, thank you.

And to Jesus Christ, who for me makes all things possible.

CYP

A NON-SILVER BASED PHOTOGRAPHIC PROCESS

by

CARY Y. PETERS

A NON-SILVER BASED PHOTOGRAPHIC PROCESS

Abstract

CARY Y. PETERS

Under the supervision of Dr. William Jensen

A film process based on the reduction of nickel (II) to elemental nickel, which is sensitive to x-ray energy photons as well as electrons, has been reported.¹

Research using this process was carried out using copper K α photons generated from an x-ray source and an electron beam from an electron microscope.

Possible advantages of this type of film process are low cost, elimination of darkroom procedures, and the stability of the exposed and unexposed film for long periods of time.

¹ NASA Tech Brief, B72-10456 (1972).

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INTRODUCTION

As an alternative to the traditional and expensive photographic process using silver salts, a new photographic type based on the deposition of elemental nickel was examined. A technical brief¹ indicated that the nickel process resembled that of the common silver deposition process. The latent image formed by irradiation of an exposed coated surface can be amplified by development to produce a permanent visible image.

The photosensitive compound on the surface coating is nickel hypophosphite, which is sensitive to x-rays and electron radiation. However, it is not sensitive to visible light. This lack of sensitivity to visible light allows processing in daylight and eliminates the need for light proof containers and darkrooms. In addition, the more abundant and less expensive nickel replaces the more costly silver used in conventional silver photographic emulsions.

HISTORICAL

Photography, as well as the chemical principles of the photographic process, have been of interest to man for a long time. Therefore, a short essay on the history, as well as the present accepted mechanisms on photography, is warranted.

The history of photography reveals a complicated pattern of evolution.² Professor J. Schultz was the first to report the effect of light on silver. He observed, in 1725, that the darkening of silver

salts was due to light and not heat. Nicephone Niepce is the man credited with the first permanent image (heliograph), using the camera obscura, in 1826. The photograph required 8 hours of exposure, and a direct positive was obtained using white bitumen.

Fox Talbot, in 1840, following suggestions from others also involved in photography, improved the process by using silver iodide and developing in gallic acid. Here, however, unlike the previous processes, prints were obtained from negatives. Talbot's process, "Tablotype," was the first one in which the latent image formed by the action of light is amplified by chemical means. This is the basic process which is still in use today.

The silver halide materials presently used generally consist of a silver halide emulsion coated on a suitable support, film base or paper. The emulsion is actually a dispersion of micron to sub-micron sized silver halide crystals (commonly called grains) in a polymer matrix, usually gelatin. The silver halides useful in photography include silver bromide and the mixed halides, especially the non-stoichiometric chlorobromides and the bromiodides. It has recently been shown that silver fluoride is photographically active,³ but this has not been commercially exploited.

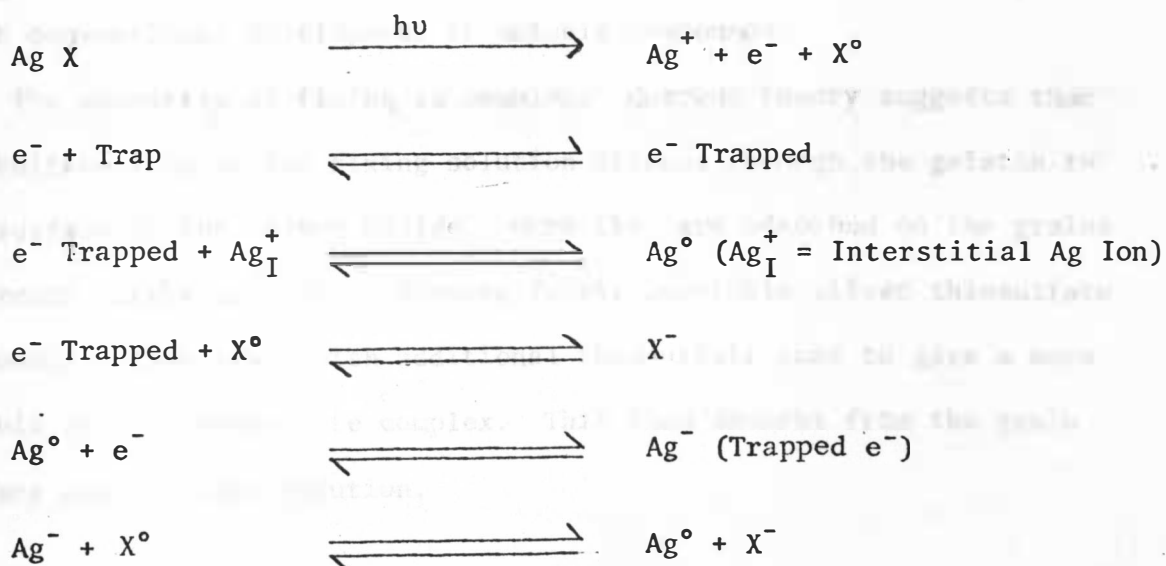
An important note to emphasize here is the role played by defects and impurities in the chemistry of the silver halide crystal. A rigorously pure, crystallographically perfect silver halide crystal would be photographically inert.⁴

Mott and Gurney's theory on latent image formation,⁵ although developed in 1938, is still the most widely accepted theory to date.

Basically the steps involved are:

1. Absorbed light liberates electrons from some bromide ions turning them into bromine atoms. The electrons then move through the crystal.
2. The electrons rapidly migrate through the crystal, but cannot leave it owing to the deflective effect of the crystal boundaries. Finally, they may lodge in electron traps in the form of crystal defects or foreign atom impurities. Such traps may be within the interior of the crystal or a sensitivity speck on its surface. Alternatively, they may recombine with the bromine atoms formed when the original bromide ions ejected electrons, thus reversing the action of light.
3. Electrons accumulating at traps such as the sensitivity speck collectively build up a negative charge. An electric field is thereby created within the crystal, and some of the interstitial silver ions migrate to the electronically charged traps. There they combine with each electron to form a larger trap for more electrons to be released by the action of light. As the silver ions are used up, the excess bromine in the crystal lattice is dissolved into the surrounding gelatin in the form of bromine atoms.

The preceeding can be expressed in the form of a sequence of reaction steps:





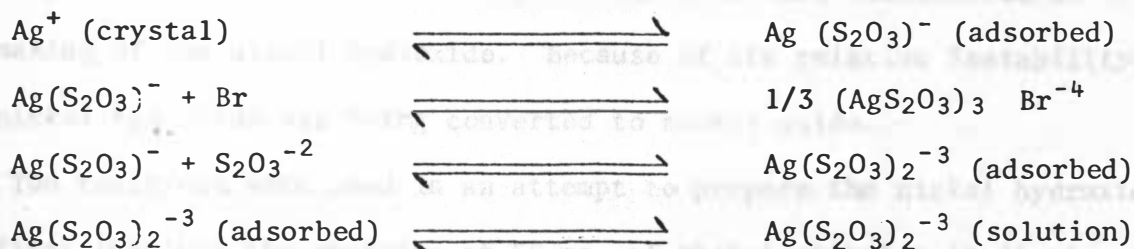
Development of the latent image can be broadly divided into two areas. In the chemical process, the developing agents are virtually electron donors, giving up electrons to the exposed silver halide grains. The atoms of silver act as catalysts attracting electrons more readily than the sensitivity specks of unexposed grains.

Physical development involves adding soluble silver (silver nitrate) to the solution with developing agents. The agents will donate electrons to the latent image specks as in chemical development. However, instead of attracting silver ions from only within each crystal itself, the silver is preferentially attracted from the solution. The latent image is therefore, in a sense, plated.

The final step in the conventional developing process is that of fixing. The purpose of fixing is to render the image permanent. This is accomplished by converting the silver halide remaining in the emulsion after conventional development to soluble compounds.

The chemistry of fixing is complex. Current theory suggests that thiosulfate ions in the fixing solution diffuse through the gelatin to the surface of the silver halide. Here they are adsorbed on the grains and react with silver ions, forming fairly insoluble silver thiosulfate compounds. They react with additional thiosulfate ions to give a more soluble silver thiosulfate complex. This then desorbs from the grain surface and out into solution.

The suggested mechanism for the chemical action of fixing is as follows:⁶



Silver halide photography has come to be the dominant imaging technology because of its high photosensitivity. This is due to the high quantum yield of electrons in an excited state in the silver halide crystal, and to the effectiveness of the latent image as a catalyst for the subsequent development reaction. There are other factors which are favorable for the silver halides among the photoconductors which have been studied.^{7,8} Several of these are:

1. Long diffusion range for the electrons in their excited state.
2. A high mobility of silver ions.
3. The ability of successively produced silver atoms to accumulate at the same spot on the crystal lattice.

EXPERIMENTAL

Initial research into nickel hypophosphite and its potential as an alternate photographic process proceeded into two broad areas. The first involved the correct formulation of a suitable photographic emulsion. The second entailed a determination of its photographic sensitivity and the quality of reproduction after exposure to radiation.

The preparation of nickel hypophosphite followed the procedure established by Rose.⁹ This called for the reaction of nickel hydroxide with hypophosphorous acid. However, difficulties were encountered in the making of the nickel hydroxide. Because of its relative instability, the nickel hydroxide was being converted to nickel oxide.

Two reactions were used in an attempt to prepare the nickel hydroxide. The first involved the reaction of 50 mg. of nickel chloride in 15 ml. of water, with a 3 normal sodium hydroxide solution.¹⁰ The second method called for 5 grams of potassium hydroxide in 50 ml. of carbon dioxide free water.¹¹ The carbon dioxide was expelled by boiling the water. This was then added dropwise to 12 grams of nickel nitrate in 50 ml. of water at 35° C. Both reactions gave products which appeared to be of uniform quality. The infrared spectra (I.R.) of both compounds indicated the products were identical.

The nickel hydroxide was added to the hypophosphorous acid solution dropwise in stoichiometric proportions. Again, the product formed was of a green non-uniform quality. Color changes from green to light green to yellow were observed when the compound was placed in an open container. The color changes were accounted for by the loss of water from the hydrated compound.

One additional method of forming the desired compound was investigated. This involved the reaction of sodium hypophosphite with nickel nitrate. Again, as in the previous results, the crystal's structure and color, as well as its I.R., indicated that the compound formed was similar to the previous one.

Because of the questionable physical appearance and texture of the nickel hypophosphite produced from the previous reaction, some doubt was cast on whether the starting material made was nickel hydroxide.

Therefore, after having exhausted the standard reaction procedures, the nickel hydroxide compound was purchased from Platz and Blatz, in an effort to make the needed nickel hypophosphite compound.

The nickel hydroxide thus obtained was added slowly with stirring to hypophosphorous acid. After a stoichiometric amount was added, no crystals were initially observed. The solution was then placed in a large water-filled container, which was insulated by styrofoam. The temperature within the insulated flask was initially set at 40° C. The water bath was then allowed to cool down slowly over several days until the temperature within the container fell to 25° C.

The crystals formed after the slow cooling process were observed under the microscope. The green crystals appeared to be well formed and of uniform texture. Again, as was observed previously, as the crystals became dehydrated on exposure to air, their color changed from green to yellow. Because of the tendency to lose water, the crystals were placed on a watch glass over a beaker of water to retard their water loss.

At this point, elemental analysis was carried out on nickel hypophosphite hexahydrate, in an attempt to verify the composition of the compound. The method used was that of using the dimethylglyoxime product as an indication of the amount of nickel present.¹²

The nickel compound was made slightly acid with acetic acid. This was then heated to 60° C, and 20 ml. of a 1 percent solution of dimethylglyoxime in ethanol was added. Ammonia was then added until the solution was slightly alkaline, and this was allowed to digest for 30 minutes at 60° C. After allowing it to stand for one hour, the solution was filtered. The product was dried at 115° C, and weighted as nickel dimethylglyoxime. This compound contained 20.3 percent nickel by weight. The results of the analysis were:

weight of nickel hypophosphite hexahydrate	-- .2211 grams
theoretical weight of nickel present	-- .044 grams
weight of nickel dimethylglyoxime	-- .2185 grams
weight of nickel present	-- .044 grams

The gravimetric nickel analysis is consistent with the formulation of nickel hypophosphite hexahydrate.

Each crystalline material produces a characteristic powder pattern, and the positions and intensities of the lines can aid in the identification of the material. Therefore, crystals were selected with the aid of a microscope, which showed good uniform texture and regular flat surfaces. They were then mounted in a Debye-Scherrer x-ray camera and exposed to x-rays for 4 hours.

The powder pattern film was developed and the major rings present were indexed. These were then compared to those reported in the literature.¹³ It was found that the two sets of data gave entirely different powder patterns. Therefore, what was previously thought to

be nickel hypophosphite hexahydrate was still in doubt and, as yet, unidentified.

A. Ferrari and C. Colla, in 1937, did an x-ray structure determination on nickel hypophosphite.¹⁴ However, the validity of their work is questioned in light of the fact that, in the literature, the structure is reported as cubic and possibly tetragonal.¹⁵

Because of these uncertainties, an attempt was initiated here to identify the formulated compound, using x-ray single crystal data.

Preliminary x-ray photographic work was carried out in an effort to procure a suitable single crystal. Weissenberg photographs indicated the crystal class of the compound as cubic.

Several satisfactory crystals were mounted on goniometer heads and taken to Iowa State University. Using the facilities of the United States Atomic Energy laboratory located there, an attempt to elucidate the correct structure was begun.

The initial photographs on several different crystals, taken on an automated diffractometer, indicated that a structure determination would not be possible. A reasonable orientation matrix could not be determined, probably because of the effects of a superlattice structure.

While efforts were being directed towards making nickel hypophosphite, the photographic properties of the compound made were also being investigated.

Following a previously determined procedure,¹⁶ formulation of a photosensitive emulsion was made. Filter paper, or in some cases, film from which its emulsion had previously been removed, were used as support.

To these a solution was applied having the following composition:

nickel hypophosphite	-- 10 grams
concentrated aqueous ammonia	-- 18 ml.
gelatin	-- 10 ml.

Following this procedure, the paper (or film) was allowed to air dry.

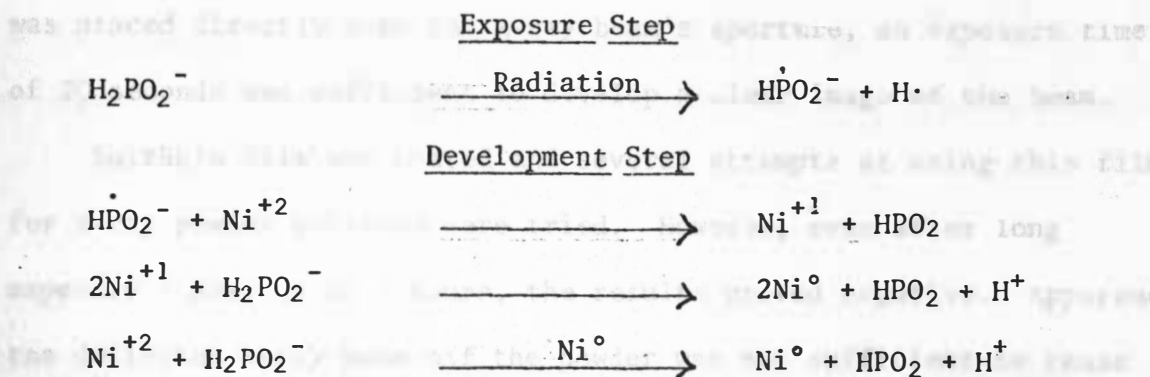
Development of the exposed film into a visible image was completed in approximately one minute. This was accomplished in an aqueous developer containing:

nickel chloride	-- 0.1 molar
sodium hypophosphite	-- 0.2 molar
ammonia	-- 1.0 molar

It was observed that a greater sensitivity of the film was obtained by use of a predevelopment in ammonia vapor. The length of time here varied slightly depending upon the length of time that the film was exposed. Usually five minutes in the vapor was sufficient to obtain this greater sensitivity.

An additional advantage here was the fact that no conventional fix was needed. Because the film is not sensitive to visible light, it is not necessary to convert the remaining nickel hypophosphite into soluble compounds.

The chemistry involved in exposing a nickel hypophosphite grain, as well as in the development of the latent image, is reported to be the following:¹⁷



The developing solution's action involves chemical as well as physical development. The sodium hypophosphite is added, so as to allow the hypophosphite anion to act as an electron donor. Additional soluble nickel, in the form of nickel chloride, is added so that it can be attracted to the exposed grain. This nickel, as well as the nickel in the emulsion surrounding the exposed grain, aid in enhancing and rendering visible the latent image.

RESULTS

Film which contained the properly formulated photographic emulsion was exposed to x-ray radiation. The voltage of the copper x-ray tube ranged from 35 to 50 kilovolts, and current ranged from 15 to 10 milliamps. Initially, the film was placed approximately a foot from the anode plate. After exposure times of 20 to 30 minutes, and following proper development, no darkening of the film was observed. As the film was brought progressively closer to the anode, the sensitivity increased, while exposure times decreased. At a distance of approximately 10 centimeters, exposure times of 2 minutes were required. When the film

was placed directly over the x-ray beam's aperture, an exposure time of 20 seconds was sufficient to develop a clear image of the beam.

Suitable film was coated and several attempts at using this film for x-ray powder patterns were tried. However, even after long exposure times; up to 6 hours, the results proved negative. Apparently, the deflected x-ray beam off the powder was not sufficient to cause exposure of the film.

At the suggestion of Dr. Granholm, work on the film's sensitivity at higher voltages was begun on the electron microscope. A voltage of 100 kilovolts was possible for the electron beam of the RCA electron microscope. Several exposures were taken with the film close to the generated electron beam. The time required for exposure dropped markedly down to six seconds.

Though the time required for exposures was decreased due to the higher voltage source, further work on the electron microscope proved difficult. The entire chamber in which the electron beam is focused, as well as the position for the film cartridge, are under an enclosed vacuum. The sensitivity of the film at varying distances from the generated electron beam could not be investigated due to the fixed position of the film cartridge.

Finally, one phase of research which was not investigated is that of sensitizing the film. The silver halide process uses silver sulfide as its sensitizer.¹⁸ It is believed that where silver sulfide has been deposited on the crystal, photo-produced electrons are attracted to the surface and, with it, the silver ions to enhance latent image formation.^{19,20}

If a substance was found to improve the sensitivity of the nickel hypophosphite film, it would greatly enhance the photographic properties of this film process.

CONCLUSION

Potential applications of this process seem to be rewarding. Thus far, NASA²¹ has applied the system to radiography. It is also applicable to diffraction and radiation detection. Other less direct applications extend into fields of mirror formation, catalysis, printed circuitry and printing. With such applications, it should find use in industry, medicine and research.

Initial work on the nickel hypophosphite film was begun because of the many advantages which this process offered. Insensitivity to visible light avoids the need for light-proof cassettes and darkrooms. Film preparation, exposure and development are carried out in daylight or under conventional illumination. The relatively more abundant and less costly nickel replaces the silver employed in conventional photographic emulsions. Shelf life, before and after exposure, because of its greater stability, simplified film handling.

The investigation of nickel as a photographic process has been discontinued. Due to its low sensitivity, it was felt that further research into one of its many potential applications could not be properly examined at this time.

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THE CRYSTAL AND MOLECULAR STRUCTURE OF

3,7-Dihydroxy-1,5-Bis(p-Bromophenyl) Octahydro-1,5-Diazocine

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3,7-Dihydroxy-1,5-Bis(p-Bromophenyl) Octahydro-1,5-Diazocine

Abstract

CARY Y. PETERS

Under the supervision of Dr. William Jensen

The structure of 3,7-dihydroxy-1,5-bis(p-bromophenyl) octahydro-1,5-diazocine has been resolved from x-ray single crystal diffraction data. The diffraction data was obtained from a four circle diffractometer (using graphite monochromated $\text{MoK}\alpha$ radiation). The crystals are monoclinic and belong to the space group $P2_1/c$. The lattice constants are a 11.35(4)Å, b 12.05(4)Å, c 16.32(7)Å, and β 97.2(2)°. Density measurements indicated four molecules per unit cell for the compound.

The structure was solved by the method of symbolic addition as the initial sign determining process. The structure was refined by the block-matrix least squares analysis. The final R factor is 10.1%, while the weighted R is 12.1%

It was shown that the hydroxyl groups prefer cis positions on the 8 membered ring, thereby affording less steric hindrance.

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type of heterocyclic ring system as the central nucleus of curare type alkaloids. Since nitrogen plays a large role in many biological processes, an understanding of the chemistry of nitrogen influenced by its lone pair of electrons would contribute significantly to the knowledge of some of these important processes.

A study of compounds in which the 1,7-position was substituted were of particular interest since these compounds provide handles by which it is feasible to synthesize new substituted, heterocyclic rings.

Attempts to prepare derivatives of octahydro-1,5-diazocine gave a product (2) which was thought to contain a mixture of cis and trans isomers. To date, from the synthesis and a suitable mechanism, there is no reason to suspect otherwise.

INTRODUCTION

For the past ten years, octahydro-1,5-diazocine (1) and its derivatives have been studied by several research groups.^{1,2,3} Interest in these compounds was stimulated when it was recognized that this



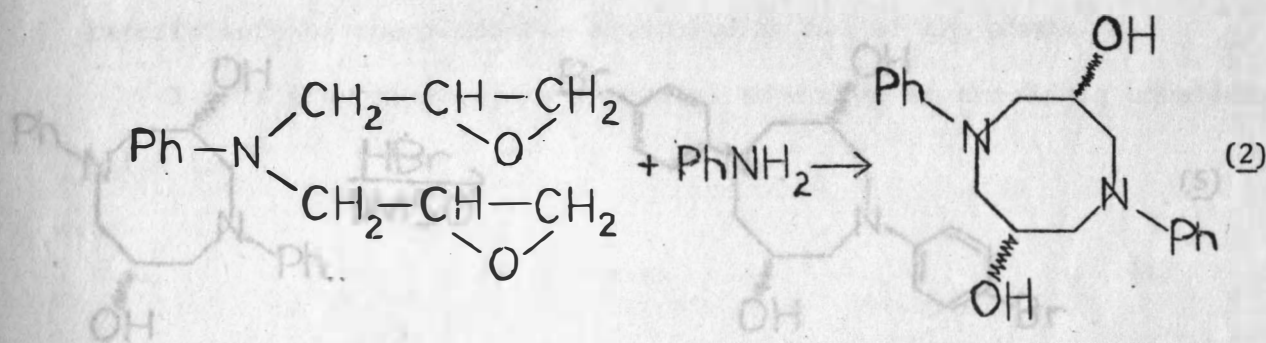
(1)

At this point the dihydroxy compound (2) reacted with PhI , followed by LiAlH_4 , to yield isomeric piperazines (3,4), both of the cis configuration. On further examination of the dihydroxy compound, it was type of heterocyclic ring system was the central nucleus of curare type alkaloids. Since nitrogen plays a large role in many biological processes, an understanding of the chemistry of nitrogen influenced by its lone pair of electrons would contribute significantly to the knowledge of some of these important processes.

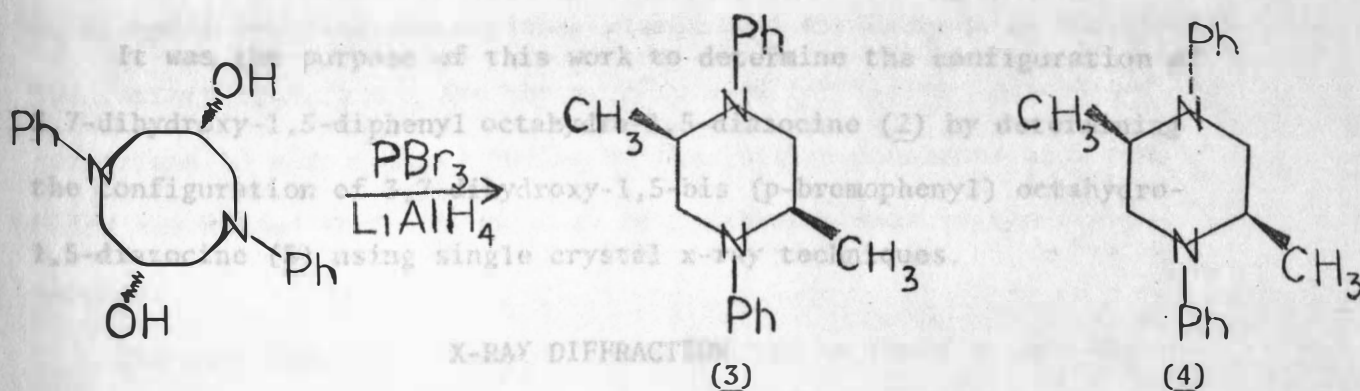
A study of compounds in which the 3,7-position was substituted were of particular interest since these compounds provide handles by which it is feasible to synthesize new unsaturated, heterocyclic rings.

Attempts to prepare derivatives of octahydro-1,5-diazocine gave a product (2) which was thought to contain a mixture of cis and trans isomers.⁴ In fact, from the equation and a suitable mechanism, there is no reason to suspect otherwise.

It was then decided to prepare a compound similar to (2) but which contained bromine. This was accomplished by dissolving (2) in DMSO and adding HBr gas.⁸

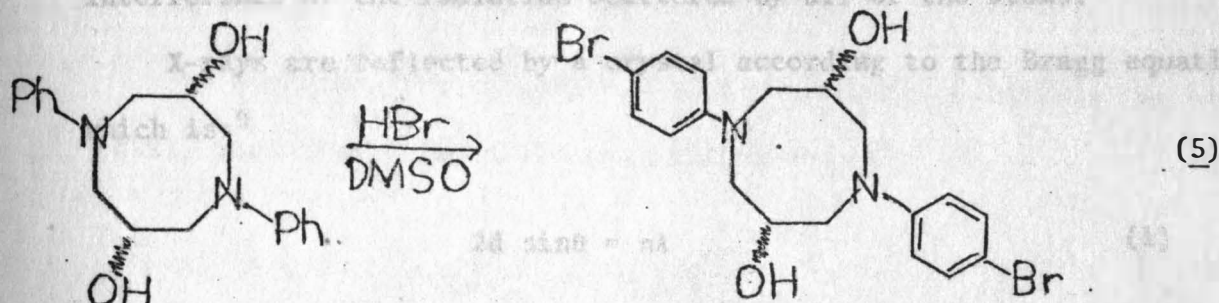


At this point the dihydroxy compound (2) reacted with PBr_3 followed by LiAlH_4 to yield isomeric piperazines (3,4), both of the cis configuration. On further examination of the dihydroxy compound, it was discovered to be only one compound but of unknown configuration.⁵



To explain the formation of (3) and (4) a mechanism was put forth which required that the starting dihydroxy compound be of the cis configuration.⁶ X-ray data was taken on the dihydroxy compound (2), but the structure has not yet been solved.⁷

It was then decided to prepare a compound similar to (2) but which contained bromine. This was accomplished by dissolving (2) in DMSO and adding HBr gas.⁸



The resulting dibromo compound (5) provided us with a compound suitable for x-ray studies.

PURPOSE

It was the purpose of this work to determine the configuration of 3,7-dihydroxy-1,5-diphenyl octahydro-1,5-diazocine (2) by determining the configuration of 3,7-dihydroxy-1,5-bis (p-bromophenyl) octahydro-1,5-diazocine (5) using single crystal x-ray techniques.

X-RAY DIFFRACTION

Because of the three-dimensional periodicity of a crystal structure, it is possible to construct sets of many planes that are parallel to each other. If an incident x-ray beam makes an angle theta with such a set of planes, the reflected beam also makes an angle theta with the planes.

Physically, the process consists of the scattering of the x-rays by the electron clouds surrounding the atoms of the crystal. The observed pattern is the result of the constructive and destructive

interference of the radiation scattered by all of the atoms.

X-rays are reflected by a crystal according to the Bragg equation which is:⁹

$$2d \sin\theta = n\lambda \quad (1)$$

The term λ is the wavelength, d is the spacing between the planes of atoms in the crystals, and θ is the angle of incidence. The angle of incidence is determined by planes of atoms in the crystal (the distance between parallel planes as well as their orientations).

Miller indices are used to catalogue reflected x-rays. In general, h , k , and l describe non-coplanar planes that are present in the crystal. The letters h , k , and l are the symbols used for Miller indices and correspond to whole number ratios of the lattice constants a , b and c , which are needed to intercept sets of parallel planes in the crystal lattice.

The distance between given planes (d) can be found in any monoclinic crystal using the following equation:¹⁰

$$1/d^2 = (h^2/a^2 + l^2/c^2 - 2hl\cos\beta/ac)/\sin^2\beta + k^2/b^2 \quad (2)$$

In the equation a , b , and c are lattice constants and the angle β is the angle between the a and c axis.

In addition to MATHEMATICAL RELATIONSHIPS

By measuring the intensities of the reflected beam from the plane (hkl), one obtains the following relationship:¹¹

$$|F(hkl)|^2 \propto I(hkl) \quad (3)$$

$F(hkl)$ is known as the structure factor. The measured intensities require corrections for the polarization of x-rays and other factors which influence the intensity. Values for $F(hkl)$ can be obtained from a set of measured intensities according to the equation:¹²

$$|F| = \sqrt{\frac{KI_{hkl}}{L_p}} \quad (4)$$

Again, F is the structure factor, I is the intensity of the x-ray beam, and K is a proportionality constant. It is common practice to give this structure factor the symbol (F_o) and call it the observed structure factor because it is derived from observed intensity data.

The L and p terms are Lorentz and polarization factors respectively; these are concerned with the relative rates at which the crystal passes through its reflecting orientation, and with the fact that the diffracted radiation is partly polarized.¹³ These are basically a simple function of the Bragg angle 2θ . For a detailed discussion of Lorentz and polarization factors, consult Nuffield.¹⁴

In addition to having a numerical value, the structure factor must have a sign corresponding to its phase. Unfortunately, the term $|F|$, as defined in equation (4) can have two values; one positive in sign and the other numerically equal but negative in sign. Only one of the signs can be correct. This apparent impasse is known as the phase problem in crystallography. Determination of the correct sign is, then, the fundamental problem of crystal structure solutions.

Atom positions in the unit cell can be used to calculate the magnitude of the structure factor, as well as its correct sign, indicating its phase. F_c is the symbol given to this structure factor and represents the calculated structure factor derived from atom positions. Calculation of F_c from atom positions is obtained from equation (5):¹⁵

$$F_c = \sum A \sin(xh+yk+zl)2\pi + B \cos(xh+yk+zl)2\pi \quad (5)$$

The letters x , y , and z represent atom coordinates in terms of unit cell parameters. The summation is over all atom positions in the unit cell. A and B are the atomic scattering factors for each individual atom, and are basically a function of the angle of reflection and the atomic number of the atom involved. If all atoms, or most of the atoms, contribute to the structure factor in the same phase, the structure factor will have a relatively high value.

From the general structure terms (and mathematical relationships), the electron density at positions x , y , and z expressed in unit cell fractions is equal to:¹⁶

be perfect. An indication of how well the two agree is calculated by the equation:

$$\rho(x,y,z) = \frac{1}{V} \sum_{hkl} (F_{hkl}) \exp[-2\pi i(hx+ky+lz)] \quad (6)$$

It then becomes possible to calculate an electron density if one knows the signs of the structure factors. The term V is the unit cell volume, and it normalizes the density in terms of electrons per cubic Ångstrom. The electron density at x , y , and z is ρ . The terms h , k , and l are integers over which the series is summed. Because of the three dimensional periodicity, a triple summation is required.

The placement of several atoms can then be used in equation (6) to deduce a crude electron-density map. This first approximation map can lead to the estimate of the position of more of the atoms. Thus, with equation (7), the signs of the structure factors of more of the diffraction results can be obtained:¹⁷

$$F(hkl) = \text{const.} \iiint \rho(x,y,z) e^{2\pi i(hx+ky+lz)} dx dy dz \quad (7)$$

The remaining atoms in the molecule can usually be located if the reflections are not counted as heavily in the calculation of the R factor. A number known as the weight, given the symbol w , is calculated for each observed structure factors are used to make an electron density map. This type of map is called a Fourier synthesis and is often used to locate atoms for the model structures.

Use of equation (5) with correct atom positions will give a value of F_c which should match in magnitude the value of F_o . However, experimental errors are involved. Therefore, no match of F_c to F_o will

be perfect. An indication of how well the two agree is calculated by the equation:¹⁸

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad (8)$$

A more valid structural model is obtained when the weighted R factor is the one which is minimized. When the R factor is sufficiently low,

the This R value is commonly called the reliability factor, and is an arbitrary measure of the correctness of a structure. Usually, diagrams

of When intensity data is collected, there will be many reflections which are only slightly above background levels. Therefore, the accuracy of these reflections is obviously questionable. A structure refined and based heavily on these types of reflections would not be a true representation of the molecule.

In an effort to compensate for the inherent errors of this type of reflection, a weighting scheme is developed whereby these types of reflections are not counted as heavily in the calculation of the R factor. A number known as the weight, given the symbol w , is calculated for each reflection. It is simply a function of the estimated standard deviation of the intensity and must be calculated for every reflection. Calculation of the weighted R factor proceeds according to the equation:

the formula used is

$$R = \frac{\sum |wF_o| - |wF_c|}{\sum |wF_o|} \quad (9)$$

The terms on the right side of the equation are from the electron density function map.

A more valid structural model is obtained when the weighted R factor is the one which is minimized. When the R factor is sufficiently low, the structure is said to be solved. From the atom coordinates, bond lengths, as well as bond angles, may be obtained. Additionally, diagrams of the molecule can now also be made.

METHODS OF SOLVING STRUCTURES

The essential steps involved in a structural solution may be classified into two broad areas. The initial step is to obtain the trial structure. After the atom coordinates are known approximately, a computer program is used which will vary the positional as well as the thermal parameters in such a way as to minimize the R factor. This procedure will vary little regardless of what method is used to obtain the trial structure.

A. L. Patterson, in 1934, developed the method which consists of constructing a map providing useful information about the structure.

The formula used is:¹⁹

$$P(x,y,z) = \sum_{hkl} |F(hkl)|^2 \cos 2\pi(hx+ky+lz) \quad (10)$$

The terms on the right side are similar to those from the electron density function equation (7). P is simply the height of the peak at coordinates x , y , and z . Since all distances between all atoms are calculated, there are many peaks. The Patterson function thus gives a map of the vectors between atoms. There is a Patterson peak for each interatomic vector.

Peaks associated with distances between symmetrically equivalent atoms are also shown. These peaks are known as Harker peaks.²⁰ They arise because the vectors between corresponding atoms of molecules related by symmetry elements have one or more constant coordinates. By finding the larger peaks, it is possible to locate the position of the more prominent atoms.

One method used quite often in solving a structure is called the heavy-atom method. A heavy atom is attached to the compound, and its position may be located from the Patterson map. From the position of the heavy atom, its contribution to the structure factor may be calculated. If the atom is heavy enough, it may by itself determine enough phases so that a Fourier map of the electron density will reveal the positions of some of the lighter atoms. On the other hand, it is desirable that the heavy atom not be too heavy. If this is the case it

may dominate the scattering to such an extent that the lighter atoms cannot be recognized on the Fourier maps. A convenient rule of thumb which has been used as a guide in the selection of a heavy atom is:²¹

Additional atom positions are located and the cycle is continued until eventually the entire structure is determined.

The number of reflections for which signs are needed to be determined, if a structure is to be solved, is arbitrary and requires a decision from the crystallographer. However, a minimum of five reflections per atom is recommended.²²

$$\frac{\Sigma(Z^2 \text{ heavy})}{\Sigma(Z^2 \text{ light})} \sim 1 \quad (11)$$

The Z, or atomic number of the heavy atom squared, should be approximately equal to the sum of the atomic number of the light atoms squared.

Therefore, the success of the heavy-atom method rests on the presence of an atom heavy enough to determine correctly the phases of a substantial number of structure factors with large magnitudes. By finding its position, the signs of most of the structure factors are calculated correctly.

One direct method, known as the symbolic addition method, can be used to obtain a trial structure. This is termed a direct method in that an attempt is made to determine the phases of the structure factors without first deducing a set of atomic positions. This method consists of determining the signs of an arbitrary number of structure factors using mathematical relationships. These structure factors with their determined signs are then used to construct an electron density map. Regions of high electron density on the map are chosen for atom positions

which can be used for calculations of structure factors. The signs of the new calculated structure factors and the magnitude of the observed structure factors are then used to construct a new electron density map. Additional atom positions are located and the cycle is continued until eventually the entire structure is determined.

The number of reflections for which signs are needed to be determined, if a structure is to be solved, is arbitrary and requires a decision from the crystallographer. However, a minimum of five reflections per atom is recommended.²²

If five reflections per atom is used as a standard, the crystal under investigation with 27 atoms per unit cell would require the signs of 135 reflections determined. These reflections have 135^2 possible sign combinations, far too many combinations to handle, even with today's high speed computers.

Symbolic addition allows one to reduce the number of sign combinations to a reasonable number so that all possible sign combinations can be tried by Fourier synthesis.

Intensity alone cannot be used as the criterion in the selection of reflections for sign determination by symbolic addition. Atoms are not point charges so the x-ray beam, when reflected, behaves as if it is not being reflected by all of the electrons in an atom. The exact amount is less than the number of electrons in the atom. The amount of the electronic charge that the x-ray beam appears to be reflected by is known as the atomic scattering factor. The scattering factor is a function of

the angle of reflection and falls off sharply as the angle of incidence increases.

The intensity of reflected x-rays, therefore, depends to a large extent on the angle of reflection. To remove the angular dependency, a normalized structure factor, E , is calculated for each reflection by the following equation:²³

$$E = \sqrt{F_o^2 / \epsilon \sum_i^n A_i^2} \quad (12)$$

The E 's are the normalized structure factors, and will vary from 1 (complete certainty) to 1/2 (complete uncertainty) when one or more of the values are zero. The term ϵ is a multiplicity factor and the summation is over all atoms in the unit cell. A is the atomic scattering factor for atom i at that angle. Thus, a high E value is the result of most of the atoms in the unit cell diffracting the x-ray beam in the same phase.

Sayre is generally credited with the first basic method of relating the signs of the reflection to each other when certain conditions of the Miller indices are met.²⁴ His general equation is:

$$S(Fhk1) = S(Fh'k'l') \cdot S(Fh-h',k-k',l-l') \quad (13)$$

Simply stated, the signs of the structure factor with indices h, k, l is probably equal to the product of the signs of $(Fh'k'l')$ and $(Fh-h',k-k',l-l')$.

The symbolic addition process depends to a large extent on probability. Reflections that are high in intensity have statistically a large number of electrons within the crystal contributing in the same phase to the structure factor. Using equation (13), if the signs of $(Fh'k'l')$ and $(Fh-h',k-k',l-l')$ are known, the calculated probability of their sum giving the algebraically correct product is:²⁵

$$P = 1/2 + 1/2 \tanh[k(|E_{hk'l} \cdot E_{h'k'l'} \cdot E_{h-h',k-k',l-l'}|)] \quad (14)$$

The E's are the normalized structure factors, and P will vary from 1 (complete certainty) to 1/2 (complete uncertainty) when one or more of the values are zero.

There exist eight reflection classes, and each is given a letter symbol for its sign. It is these letter symbols which are used for sign determinations. The letter represents its true sign which may, in the beginning, be plus or minus. With the aid of equation (13), other signs may be determined. However, using eight letter symbols, there are still 8^2 possible sign combinations, as yet too large a quantity to deal with.

We may take any reflection and arbitrarily determine its sign.

This amounts to fixing the phases of all other reflections in this class. In a primitive monoclinic system, three symbols may be assigned arbitrary signs to fix the origin of the unit cell. The selection of the three reflections may be done by "parity arithmetic."²⁶ Once a few signs have been determined, equation (13) can be used to generate more signs, and

these in turn can be used to produce more, until a sufficient number of signs have been determined.

With the aid of a table which counts the number of times the sign combinations are in conflict, the less likely possibilities are eliminated. From those which are favorable (having few contradictions), Fourier maps are produced until one which gives recognizable molecular fragments can be observed.

After the trial structure is obtained, final refinement of the structure can proceed. Refinement is usually carried out by a computer program. The program minimizes the R factor and will determine standard deviations for all cell parameters. Following the accurate location of the atom positions, diagrams and models can then be prepared to obtain an accurate representation of the molecule.

Reflections with $I < 3\sigma$ were not used in the refinement. No absorption or dispersion correction was necessary.

DATA REDUCTION

A weighting scheme based on counter statistics²³ was applied.

Intensity data collected from the diffractometer represents the raw material from which crystal structures are deduced. Data reduction refers to the process which takes these intensities and converts them to a corrected, more usable form.

The raw data obtained from the diffractometer and then placed on computer cards are the Miller indices h , k , and l . Along with these are the angles χ , ϕ , and θ , and the net count from the intensity reading. This is obtained by merely subtracting the background count from a particular reflection.

The output from the data-reduction program consists of a disk record, one to a reflection, containing the information which will be needed for subsequent calculations. This includes the sine of theta over lambda ($\sin \theta/\lambda$), the observed structure factors and their squares. Additionally, the standard deviations for the net intensity of a reflection, as well as the standard deviation of the observed structure factor, is calculated.

Standard deviations were obtained from counter statistics where C_T and C_B represent the total background counts, respectively, and the factor 0.03 represents an estimate of non-statistical errors:

$$\sigma_I^2 = C_T + C_B + (0.03C_T)^2 + (0.03C_B)^2 \quad (15)$$

Reflections with $I < 3\sigma_I$ were not used in the refinement. No absorption or dispersion correction was deemed necessary.

A weighting scheme based on counter statistics²⁷ was applied.

The weight factors for each reflection are:

$$w = 1/\sigma^2_{F_0} \quad (16)$$

The term F is calculated by the computer using the following equation:²⁸

$$\sigma_{F_0} = \frac{1}{2} \frac{k}{\sqrt{Lp}} \frac{\sigma_I}{\sqrt{I}} \quad (17)$$

The first step is that of centering the crystal on the diffractometer. The program SETTER is used for this purpose. The angles 2θ , ω , λ , and ϕ are

The term σ_I is the standard deviation of the intensity. The other terms have the same meaning as in equation (4).

One of the major functions of the output from the data reduction program is as an input to the structure-factor program. To carry this out it is necessary to know the x-ray scattering power for each kind of atom in the cell.

The scattering power of a given atom for a given reflection is known as its scattering factor (f). This is expressed in terms of the scattering power of an equivalent number of electrons located at the atomic nucleus.²⁹

The scattering power is a function of the atom type and $\sin \theta/\lambda$. The scattering factors for hydrogen atoms were obtained in tabular form from the "International Tables for X-ray Crystallography."³⁰ Non-hydrogen atomic scattering factors were given by Hanson *et al.*³¹

DIFFRACTOMETER DATA

A suitable crystal of 3,7-dihydroxy-1,5-bis(p-bromophenyl) octahydro-1,5-diazocine was taken to Iowa State University, mounted on their computer-controlled, four circle diffractometer, and intensity data was collected.

ALICE (Ames Laboratory Integrated Crystallographic Evaluator) is the version of the indexing routine written for their computer system.

A short description of ALICE and information obtained from the program is in order.³²

The first step is that of centering the crystal on the diffractometer.

The program SETTER is used for this purpose. The angles 2θ , ω , χ , and ϕ are

designated by 1, 2, 3, and 4 respectively. By merely typing in an angle position, the crystal is rotated to the specified position. New positions are typed in (usually by rotations of 90°) until the crystal is aligned on the crosshairs of the diffractometer telescope. When the crystal is properly centered, a negative number is entered to cause this routine to terminate.

The second step asks for the wavelength used, the molecular weight and density of the compound. A polaroid cassette is then mounted on the diffractometer, and several omega oscillation photographs are taken. Omega oscillation photographs with $\chi = 0$ and $\phi = 0, 30, 60, 90, 120$, and 150 are usually adequate for a proper cell orientation. Ten to fifteen oscillations are usually taken so that good quality pictures can be obtained. If enough oscillation photographs have been taken, N is typed in, and the routine proceeds to the next step.

The third step asks for χ , ϕ , D and A values. The χ and ϕ values are those associated with the oscillation photographs that were taken. D represents the radial distance and is measured from the reflection to a center point made via a small hole in the beam stop. A is the angle in degrees appropriate for the particular reflection and is measured counterclockwise from the right horizontal.

After χ , ϕ , D and A values are input, 2θ and λ values for the reflection are computed. It then searches for the omega value by scanning through the range between -10 to $+10$ degrees in omega and looking for the reflection "on the fly" at 3 degrees per second. If a peak of reasonable size can be found, the omega value will then be typed out.

If the search doesn't reveal a peak significantly above background, χ will be offset by -1 and then by -2 degrees, then by +1 and finally by +2 degrees from the initial value and the omega search repeated for each of the cases. If the reflection peak is found in any of these passes, the omega value will be printed out. If no peak can be found, the reflection will be rejected at this point. The process of inputting reflections is continued until an appropriate number (12 or so) have been found, after which time the program is terminated.

The computer then takes the approximate χ , ϕ , ω and 2θ values and "tunes" in on these in an effort to obtain more accurate angular values. Once the reflections have been tuned, the actual indexing begins. For a thorough discussion on the indexing procedure, Jacobson³³ should be consulted. The error limit, which is an indication of how well aligned the diffractometer is, will be determined. The program types out this error limit followed by the reduced cell volume, and reduced cell scalars. Next the unit cell parameters followed by indices that have been determined by the indexing procedure of the original reflections, are printed out. The orientation matrix, as well as the number of molecules per cell, are also determined in this part of the program.

If one is satisfied with the cell that is obtained, oscillation photographs about the a, b, and c axes are taken to verify that no layers have been missed. Also mirror symmetry elements which may be present may be observed to verify the crystal system that has been indicated via the reduced cell scalars.

After this step has been completed and the first cell that is obtained is the appropriate cell for the crystal, the program ALICE is completed. Now one is ready to initiate the data collection program. Although the orientation matrix produced by ALICE is not highly accurate, due to the low angle reflections that are used, it is generally sufficient to allow one to readily find standard reflections to be used in the data collection routine.

Standard selection involves selection of higher angle reflections with high intensities to serve as standards for subsequent data collection. Three standards are selected which will define the cell. The standards are then returned to after every 75 reflections, from which one can determine if the crystal has undergone any decomposition under the x-ray beam, or if it has moved its position on the goniometer head.

The data collection procedure is all computer controlled, so that the crystal is rotated to the needed Miller indices automatically. Initially, the Miller indices h and k are kept constant and l is allowed to increase. Then k is increased till its limit is reached; finally the same routine is followed by h . The program also collects intensity readings for reciprocal space in a similar manner.

The mode of measurement on the four-circle diffractometer is to offset ω and 2θ , make a background measurement, and then go to the peak top to obtain its intensity. It will do this for all the reflections and may discard a reflection if its intensity is only marginally above background. The net intensity is merely the total

intensity reading minus the intensity reading from the background.

PRELIMINARY

Crystals suitable for an x-ray single crystal structure analysis were obtained by recrystallization from a toluene-ethanol solvent. The solution was placed in a sample bottle and the solvent was allowed to slowly evaporate until suitable crystals were obtained.

The resulting crystals were rectangularly shaped with approximate dimensions of 0.2 X 0.6 X 0.3 mm. The space group $P2_1/c$ was deduced from systematic absences obtained from diffractometer data.

From density and unit cell volume measurements, four molecules were determined to be present per unit cell. The symmetry equivalent positions in this unit are:³⁴ (1) x, y, z ; (2) $-x, -y, -z$; (3) $x, 0.5-y, 0.5+z$; (4) $-x, 0.5+y, 0.5-z$. The calculated density is 1.52 g/cm^3 , while the observed density is 1.47 g/cm^3 (determined by the flotation method utilizing an ethylene bromide and methanol solution).³⁵

Diffractometer data yielded 4277 independent reflections of which 1719 were above three estimated standard deviations of their intensity. These 1719 reflections were used for the final structure refinement.

Eleven high angle reflections were centered at two theta and minus two theta and accurate lattice constants were determined using computer programs available at Iowa State University.

Following the placement of all the atoms with isotropic thermal parameters and one cycle of least squares calculations, R fell from

SOLVING THE STRUCTURE

First attempts to solve the structure proceeded through generation of a Patterson map from the intensity data. Using reasonable combinations (approximately 9), several possible bromine positions were located. However, upon using these positions as trial models, they were unsuccessful in developing the atom positions of recognizable molecular fragments on Fourier maps.

The method of symbolic addition was used to confirm the positions of the bromine atoms. Eight symbols (A-H) were used for the starting set. Three of these (A, C, E) were arbitrarily assigned as origin-fixing reflections. One of the signs (F) was used infrequently in building up the set of signed structure factors, so that it was discarded. After five iterations the signs of 165 reflections were determined.

With the aid of a contradiction table, which counts how many times each sign combination is in conflict, four electron density maps were generated which had no contradictions.

The electron density map in which the symbols all had positive signs was found to be consistent with the Patterson map. After two carbon atoms were placed in the trial model, R fell to 0.51, from which the entire molecule was observed.

REFINEMENT

Following the placement of all the atoms with isotropic thermal parameters and one cycle of least squares calculations, R fell from

0.51 to 0.25. Because of the large number of atoms in the molecule, only half of the structure could be refined with anisotropic thermal parameters during a least squares cycle. Therefore, half of the structure's parameters were kept constant and the other half were allowed to vary. The same was done for the other portion of the molecule also, causing R to fall to only 0.24.

At this point a difference map was generated to see if there were any atoms which were not placed, but were present in the structure. It was found that three atoms were not included which were part of the molecule. From the relative size of the peaks present on the difference map, the atoms were suspected to be two carbons and an oxygen.

Evidently an ethanol molecule had hydrogen bonded to one of the hydroxides on the diazocine ring during recrystallization. The position of the ethanol molecule was determined, placed in the least squares calculation along with the rest of the molecule isotropically, diminishing R to 0.15.

After two full cycles, with half of the molecule being varied anisotropically at a time, R fell to 0.136. Because the positions of the atoms in the ethanol molecule were still varying to a great extent, they were kept isotropic. However, following three isotropic cycles, they were allowed to become anisotropic, resulting in R dropping to 0.107.

The positions of all the hydrogen atoms, except those on the end carbon of the ethanol molecule, were determined with the aid of a difference map. The positional coordinates of the hydrogen atoms were

allowed to vary, while their temperature factors were held constant.

Following two cycles, in which only the hydrogen atoms varied and the rest of the atom's positions were fixed, R became 0.104.

Finally, half of the molecule, including the hydrogen atoms, were varied, again with their temperature factors held constant. The same procedure was followed for the other half of the molecule, resulting in a final R of 0.101 with a weighted R of 0.121.

SUMMARY

Single crystals of 3,7-dihydroxy-1,5 bis(parabromophenyl) octahydro-1,5-diazocine were grown and subsequently used to obtain a set of x-ray intensity data. The systematically absent reflections that were revealed from the intensity data were used to determine the space group.

The unit cell translations and angles were initially obtained from intensity data, and refined using eleven high angle reflections.

The structure was solved by the direct method of symbolic addition. The signs of 165 structure factors were initially determined; these were then used to generate electron density maps. The fourth electron density map, in which the signs of all the structure factors were positive, revealed the bromine positions consistent with the Patterson map.

The remaining atom positions were found from electron density maps and were refined by the block-matrix least squares fitting process. Difference Fourier maps followed by least squares adjustment of atom

parameters was used to locate the hydrogen atoms.

From the final atom positions for the structure, a molecular diagram was made using the computer program ORTEP.³⁶ A computer was used to accurately calculate bond lengths and bond angles. All atom positions had estimated standard deviation values calculated from the block-matrix refinement. These standard deviation values were then used to calculate standard deviations in bond lengths and bond angles.

Elucidation of the 3,7-dihydroxy-1,5-bis(p-bromophenyl) octahydro-1,5-diazocine indicated that oxygen atoms were of the cis configuration. A molecule of ethanol was hydrogen-bonded to oxygen atom 1. This would not interfere with the stereochemistry about the number 3 atom. Since the preparation of the title compound from 3,7-dihydroxy-1,5 diphenyl octahydro-1,5-diazocine did not affect the stereochemistry about the 3,7 positions the configuration of 3,7-dihydroxy-1,5 diphenyl octahydro-1,5-diazocine must also be cis.

Br(1)	313(2)	2023(1)	7854(1)
Br(2)	8877(2)	1483(1)	109(1)
C(1)	3299(12)	712(2)	718(1)
C(2)	1917(14)	444(3)	6143(9)
C(3)	2604(13)	-527(13)	660(3)
C(4)	2675(12)	-1232(12)	7307(8)
C(5)	2087(14)	-917(14)	7956(10)
C(6)	1352(15)	394(15)	7909(9)
N(1)	3328(10)	3279(10)	7366(7)
C(7)	3988(14)	-2524(14)	6673(10)
C(8)	5171(13)	-1839(13)	6684(8)
O(1)	5305(9)	-2037(7)	3843(5)
C(9)	5144(13)	-2569(13)	7246(8)
N(2)	6082(10)	-2130(10)	8137(6)
C(10)	3504(12)	-3396(12)	8645(9)
C(11)	4735(13)	-2745(14)	8779(8)
O(2)	1891(10)	-3424(10)	9458(6)
C(12)	3288(14)	-2927(12)	8052(8)

Table 1

Positional Parameters of the Nonhydrogen Atoms

Atom	(x 10 ⁴)		
Atom	x	y	z
Br(1)	313(2)	2029(2)	7094(1)
Br(2)	8977(2)	1499(2)	-109(1)
C(1)	1299(12)	719(12)	7186(9)
C(2)	1917(14)	444(14)	6543(9)
C(3)	2604(13)	-527(13)	6601(9)
C(4)	2675(12)	-1252(12)	7307(8)
C(5)	2057(14)	-917(14)	7956(10)
C(6)	1352(15)	36(15)	7909(9)
N(1)	3328(10)	-2226(10)	7366(7)
C(7)	3988(14)	-2524(14)	6673(10)
C(8)	5171(13)	-1969(13)	6684(8)
O(1)	5505(9)	-2037(7)	5843(5)
C(9)	5144(13)	-2569(13)	7246(8)
N(2)	6082(10)	-2330(10)	8147(6)
C(10)	5504(12)	-3096(12)	8645(9)
C(11)	4235(13)	-2748(14)	8779(8)
O(2)	3891(10)	-3424(10)	9458(6)
C(12)	3268(14)	-2999(12)	8062(8)

Table 1 (continued)

Atom	x	y	z
C(13)	6702(12)	-1422(12)	8530(8)
C(14)	7386(12)	-695(11)	8081(8)
C(15)	8065(13)	175(13)	8470(9)
C(16)	8027(12)	343(11)	9339(8)
C(17)	7328(14)	-298(14)	9795(9)
C(18)	6665(15)	-1199(15)	9392(9)
O(3)	7165(10)	-482(8)	5681(6)
C(19)	8439(15)	-324(14)	5830(12)
C(20)	8997(19)	-1410(18)	5784(13)

H(9)

H(10)

H(11)

H(12)

H(13)

H(14)

H(15)

H(16)

H(17)

H(18)

H(19)

Table 2

Positional Parameters of the Hydrogen Atoms

(x 10³)

Atom	x	y	z
H(1)	263(14)	76(14)	633(10)
H(2)	291(14)	-72(14)	600(10)
H(3)	203(14)	-117(13)	858(10)
H(4)	100(14)	27(14)	820(10)
H(5)	390(15)	-318(13)	671(11)
H(6)	348(15)	-248(14)	617(11)
H(7)	521(13)	-95(15)	675(9)
H(8)	697(15)	-210(14)	687(10)
H(9)	708(15)	-262(14)	733(10)
H(10)	621(15)	-314(14)	907(11)
H(11)	572(15)	-317(14)	949(10)
H(12)	425(14)	-200(14)	907(10)
H(13)	414(16)	-326(14)	-19(9)
H(14)	254(15)	-296(14)	823(10)
H(15)	359(14)	-393(15)	787(9)
H(16)	747(14)	-55(13)	748(10)
H(17)	872(13)	-81(14)	816(9)
H(18)	727(14)	-42(13)	44(10)
H(19)	578(14)	-147(13)	956(10)

Table 2 (continued)

Temperature Parameters of the Nonhydrogen Atoms

Atom	$x \times 10^3$			y			z
H(20)	893(14)			23(13)			656(9)
H(21)	904(14)			11(13)			546(10)
Br(1)	125(2)	91(1)	82(1)	2(1)	-7(1)	1(1)	
Br(2)	179(3)	131(2)	63(1)	-68(2)	7(2)	-10(2)	
C(1)	70(15)	69(25)	72(9)	19(15)	-5(17)	-10(9)	
C(2)	96(17)	116(17)	47(7)	-12(14)	6(10)	5(10)	
C(3)	91(18)	96(16)	43(8)	-10(14)	-34(10)	5(10)	
C(4)	84(16)	97(16)	27(8)	-16(14)	4(9)	15(9)	
C(5)	92(16)	119(16)	47(8)	-17(14)	-11(10)	-4(10)	
C(6)	170(19)	108(17)	46(8)	-27(16)	14(15)	2(10)	
H(1)	91(14)	97(14)	38(6)	-7(12)	-12(7)	4(8)	
C(7)	104(16)	106(15)	40(7)	-16(14)	10(9)	-15(9)	
C(8)	95(17)	88(16)	57(8)	-1(15)	3(13)	-21(9)	
O(1)	145(12)	88(10)	26(4)	2(9)	19(5)	-14(4)	
C(9)	93(16)	106(16)	23(7)	15(14)	15(10)	-4(9)	
N(2)	98(14)	95(14)	35(6)	-21(12)	7(8)	-3(3)	
C(10)	71(16)	80(15)	48(8)	-43(13)	8(10)	8(9)	
C(11)	103(27)	117(18)	53(7)	-11(15)	19(10)	17(10)	
O(2)	134(12)	120(11)	38(4)	-16(10)	20(5)	9(6)	

Table 3

Temperature Parameters of the Nonhydrogen Atoms

(x 10 ⁴)						
Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Br(1)	125(2)	94(1)	87(1)	8(1)	-7(1)	1(1)
Br(2)	179(3)	131(2)	63(1)	-59(2)	3(1)	-10(1)
C(1)	70(15)	69(15)	72(9)	19(13)	-3(10)	-10(9)
C(2)	96(17)	118(17)	47(7)	-12(14)	6(10)	5(10)
C(3)	91(18)	96(16)	42(8)	-15(14)	-3(10)	5(10)
C(4)	84(16)	97(16)	27(8)	-16(14)	4(9)	15(9)
C(5)	92(16)	110(16)	47(8)	-17(14)	-1(10)	-4(10)
C(6)	120(19)	108(17)	46(8)	-27(16)	3(10)	2(10)
N(1)	91(14)	97(14)	38(6)	-7(12)	-1(8)	4(8)
C(7)	104(16)	105(15)	40(7)	-16(14)	19(9)	-13(9)
C(8)	95(17)	88(16)	37(8)	-1(14)	2(10)	-21(9)
O(1)	145(12)	88(10)	26(4)	1(9)	19(6)	-14(6)
C(9)	93(16)	108(16)	23(7)	15(14)	13(19)	-4(9)
N(2)	98(14)	98(14)	35(6)	-21(12)	7(8)	-3(8)
C(10)	71(16)	80(15)	48(8)	-13(13)	8(10)	8(9)
C(11)	103(17)	117(18)	33(7)	-11(15)	19(10)	17(10)
O(2)	134(12)	120(11)	35(4)	-16(10)	20(6)	9(6)

Table 3 (continued)

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
C(12)	109(18)	58(14)	33(7)	-16(13)	-8(10)	15(8)
C(13)	103(15)	94(17)	30(8)	25(16)	15(10)	23(10)
C(14)	90(17)	73(15)	36(8)	4(14)	3(10)	13(10)
C(15)	108(19)	107(20)	38(10)	8(17)	9(11)	2(11)
C(16)	89(18)	54(14)	49(9)	-10(13)	2(11)	-1(9)
C(17)	113(20)	130(19)	40(8)	-49(17)	13(11)	-16(11)
C(18)	119(21)	143(22)	43(10)	-6(19)	8(12)	1(12)
O(3)	139(15)	91(12)	71(6)	-18(11)	14(8)	-2(7)
C(19)	119(24)	96(20)	79(10)	7(19)	6(13)	-48(12)
C(20)	186(26)	131(24)	70(12)	33(22)	10(14)	-6(14)

Anisotropic temperature factors are in the form:

$$\exp - 10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$$

Table 4
Interatomic Distances (\AA)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Br(1)	C(1)	1.93(1) \AA	C(8)	C(9)	1.53(2) \AA
Br(2)	C(16)	1.91(1)	C(9)	H(8)	1.1(2)
C(1)	C(2)	1.38(2)	C(9)	H(9)	1.2(2)
C(1)	C(6)	1.43(2)	C(9)	N(2)	1.51(2)
C(2)	H(1)	1.0(1)	N(2)	C(13)	1.40(2)
C(2)	C(3)	1.40(2)	N(2)	C(10)	1.43(2)
C(3)	H(2)	1.1(2)	C(10)	H(10)	1.1(1)
C(3)	C(4)	1.44(2)	C(10)	H(11)	1.3(2)
C(4)	N(1)	1.39(2)	C(10)	C(11)	1.52(2)
C(4)	C(5)	1.40(2)	C(11)	H(12)	1.0(1)
C(5)	H(3)	1.1(2)	C(11)	O(2)	1.46(2)
C(5)	C(6)	1.41(2)	C(11)	C(12)	1.53(2)
C(6)	H(4)	1.0(2)	O(2)	H(13)	1.0(2)
N(1)	C(12)	1.48(2)	C(12)	H(14)	0.9(1)
N(1)	C(7)	1.48(2)	C(12)	H(15)	1.0(1)
C(7)	H(5)	1.2(2)	C(13)	C(14)	1.41(2)
C(7)	H(6)	1.0(2)	C(13)	C(18)	1.43(2)
C(7)	C(8)	1.49(2)	C(14)	H(16)	0.9(2)
C(8)	H(7)	1.0(1)	C(14)	C(15)	1.40(2)
C(8)	O(1)	1.46(2)	C(15)	H(17)	1.42(2)

Table 5

Interatomic Angles

N(2)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)	
Br(1)	C(1)	C(2)	119(1) °	O(1)	C(8)	C(9)	106(1) °
Br(1)	C(1)	C(6)	120(1)	O(1)	C(8)	H(7)	117(9)
C(2)	C(1)	C(6)	121(1)	C(9)	C(8)	H(7)	112(8)
C(1)	C(2)	C(3)	119(1)	C(8)	C(9)	N(2)	112(1)
C(1)	C(2)	H(1)	133(8)	N(2)	C(9)	H(8)	115(8)
C(2)	C(3)	C(4)	123(1)	N(2)	C(9)	H(9)	96(8)
C(2)	C(3)	H(2)	109(7)	C(9)	N(2)	C(10)	119(1)
C(3)	C(4)	C(5)	117(1)	C(9)	N(2)	C(13)	121(1)
C(3)	C(4)	N(1)	123(1)	C(10)	N(2)	C(13)	120(1)
C(5)	C(4)	N(1)	120(1)	N(2)	C(10)	C(11)	116(1)
C(4)	C(5)	C(6)	122(1)	N(2)	C(10)	H(11)	114(8)
C(6)	C(5)	H(3)	102(6)	C(11)	C(10)	H(10)	93(6)
C(1)	C(6)	C(5)	119(1)	C(10)	C(11)	O(2)	109(1)
C(5)	C(6)	H(4)	105(7)	C(10)	C(11)	C(12)	114(1)
C(4)	N(1)	C(7)	118(1)	C(10)	C(11)	H(12)	113(6)
C(4)	N(1)	C(12)	121(1)	O(2)	C(11)	C(12)	103(1)
C(7)	N(1)	C(12)	121(1)	C(11)	O(2)	H(13)	113(8)
N(1)	C(7)	C(8)	115(1)	N(1)	C(12)	C(11)	112(1)
N(1)	C(7)	H(5)	110(10)	N(1)	C(12)	H(14)	109(9)
C(8)	C(7)	H(6)	104(12)	N(1)	C(12)	H(15)	104(8)
C(7)	C(8)	O(1)	107(1)	C(11)	C(12)	H(14)	115(9)
C(7)	C(8)	C(9)	112(1)	C(11)	C(12)	H(15)	111(7)
C(7)	C(8)	H(7)	102(6)	N(2)	C(13)	C(14)	122(1)

Table 5 (continued)											
N(2)	C(13)	C(18)	121(1) ^o	C(15)	C(16)	C(17)	120(1) ^o				
C(14)	C(13)	C(18)	117(1)	C(16)	C(17)	C(18)	120(1)				
C(13)	C(14)	C(15)	122(1)	C(16)	C(17)	H(18)	115(7)				
C(13)	C(14)	H(16)	121(7)	C(18)	C(17)	H(18)	123(7)				
C(14)	C(15)	C(16)	119(1)	C(13)	C(18)	C(17)	121(1)				
C(14)	C(15)	H(17)	126(8)	C(17)	C(18)	H(19)	123(8)				
C(16)	C(15)	H(17)	115(8)	O(3)	C(19)	C(20)	108(1)				
Br(2)	C(16)	C(15)	120(1)	C(20)	C(19)	H(20)	93(7)				
Br(2)	C(16)	C(17)	119(1)	C(20)	C(19)	H(21)	94(12)				

Table 6

OBSERVED AND CALCULATED STRUCTURE FACTORS

H,K= 0, 0	11	35	35	9	17	13	10	10	11	H,K= 1, 9	7	28	30
L FOB FCA	12	9	8	H,K= 0, 10	11	9	8	L FOB FCA	8	4	4		
2 52 52	13	7	9	L FOB FCA	12	2	4	0 11 10	9	26	22		
4 72 78	14	5	8	2 40 34	14	13	12	1 4 4	10	24	24		
6 46 46	H,K= 0, 5	5	3	7	H,K= 1, 4	2	22	21	11	8	9		
8 25 23	L FOB FCA	6	7	9	L FOB FCA	3	5	7	12	3	5		
10 31 31	1 43 37	H,K= 0, 11	0	33	34	6	28	25	13	16	16		
12 7 7	2 17 17	L FOB FCA	1	52	52	H,K= 1, 10	14	2	5				
14 25 28	3 47 44	1 2 5	2	43	39	L FOB FCA	0	7	5	L FOB FCA			
H,K= 0, 1	4 18 17	2 4 4	3	13	11	0 7 5	1	2	5	1 60 58			
L FOB FCA	5 32 28	3 3 5	4	4	6	1 2 5	2	29	23	2 53 55			
1 18 19	6 18 13	4 12 11	5	43	42	2 29 23	3	2	2	3 9 9			
2 40 43	7 33 33	H,K= 1, 0	6	22	19	3 2 2	5	4	4	5 51 49			
3 65 65	8 6 7	L FOB FCA	7	40	35	H,K= 1, 11	8	8	8				
4 82 79	9 13 13	0 46 54	8	37	32	L FOB FCA	9	21	21				
5 60 52	10 23 22	2 32 39	9	3	2	0 2 3	10	9	11				
6 31 30	12 29 27	4 147 151	11	28	28	2 18 18	11	15	15				
7 50 47	H,K= 0, 6	6 22 23	12	15	16	H,K= 2, 0	12	4	5				
8 28 26	L FOB FCA	8 25 22	13	2	6	L FOB FCA	13	17	15				
9 14 16	0 37 36	10 31 28	14	4	6	0 9 10	H,K= 2, 5						
11 14 15	1 49 49	12 10 8	H,K= 1, 5	0	49	46	L FOB FCA	2 27 21	L FOB FCA				
12 3 5	2 63 54	L FOB FCA	0 20 21	1	2	5	4 3 6	0 46 43					
14 38 39	3 41 37	0 20 21	1 38 39	2	49	47	6 32 34	1 11 11					
15 9 9	4 24 22	1 38 39	2 16 17	3	2	3	8 2 1	2 46 44					
H,K= 0, 2	5 8 6	2 16 17	3 47 42	4	57	54	10 4 6	3 10 11					
L FOB FCA	6 21 19	3 47 42	5 115 123	5	47	44	12 17 18	4 38 40					
0 97 97	7 3 2	5 17 14	6 15 15	7	17	15	H,K= 2, 1	5 29 28					
1 6 6	8 14 11	6 15 15	7 16 6	8	85	80	L FOB FCA	6 37 37					
2 65 64	9 6 7	7 16 6	8 3 6	9	3	6	0 16 18	7 22 22					
3 28 25	10 2 3	8 3 6	9 3 6	10	7	7	1 21 21	8 36 36					
4 37 39	11 5 9	9 3 6	10 7 7	11	14	12	2 62 60	9 33 31					
5 16 16	12 2 4	10 7 7	11 14 12	12	20	20	3 5 9	10 10 9					
6 7 7	13 25 24	11 14 12	12 20 20	13	2	2	4 67 64	11 13 13					
7 30 28	H,K= 0, 7	12 20 20	13 2 2	14	8	8	5 16 17	12 2 7					
8 6 5	L FOB FCA	14 8 8	15 12 11	15	4	16	6 14 12	H,K= 2, 6					
9 19 20	1 60 53	15 4 16	16 15 15	16	5	15	7 21 21	L FOB FCA					
10 27 27	2 3 5	16 15 15	17 6 6	17	9	3	8 61 58	0 26 25					
11 33 34	3 13 11	17 6 6	18 8 8	18	3	5	9 16 16	1 10 9					
12 3 6	4 31 29	18 8 8	19 3 4	19	4	16	10 11 9	2 19 15					
15 4 5	5 50 43	19 3 4	20 4 16	20	5	12	12 27 27	3 70 61					
H,K= 0, 3	6 9 8	20 4 16	21 5 12	21	6	11	13 5 7	5 16 16					
L FOB FCA	7 4 7	21 5 12	22 6 15	22	7	14	14 15 14	6 15 12					
1 9 8	8 7 8	22 6 15	23 7 14	23	8	16	H,K= 2, 2	7 22 19					
2 23 23	9 29 25	23 7 14	24 8 8	24	9	17	L FOB FCA	8 22 20					
3 96 98	10 12 13	24 8 8	25 9 11	25	10	18	0 138 155	9 8 8					
4 3 2	H,K= 0, 8	25 9 11	26 10 10	26	11	19	1 156 175	10 3 5					
6 10 12	L FOB FCA	26 10 10	27 11 13	27	12	12	2 34 35	11 3 5					
7 80 80	0 20 22	27 11 13	28 12 12	28	13	15	3 1 3	12 10 11					
8 7 8	1 10 12	28 12 12	29 13 15	29	14	17	4 10 10	H,K= 2, 7					
10 3 4	2 26 22	29 13 15	30 14 16	30	15	18	5 88 86	L FOB FCA					
11 23 22	3 15 16	30 14 16	31 15 17	31	16	19	6 21 21	1 5 6					
12 8 7	4 2 4	31 15 16	32 16 18	32	17	20	7 18 18	3 9 9					
13 10 10	5 8 6	32 16 18	33 17 15	33	18	21	9 26 24	4 1 4					
14 7 7	6 2 3	33 17 15	34 18 18	34	19	22	10 3 7	5 24 23					
H,K= 0, 4	7 10 8	34 18 18	35 19 17	35	20	23	11 19 21	7 27 26					
L FOB FCA	8 14 15	35 19 17	36 20 20	36	21	24	12 13 12	8 22 17					
0 23 24	9 10 11	36 20 20	37 21 21	37	22	25	14 9 1	9 26 24					
1 60 62	10 3 6	37 21 21	38 22 22	38	23	26	H,K= 2, 3	11 10 9					
2 87 86	H,K= 0, 9	38 22 22	39 23 23	39	24	27	L FOB FCA	H,K= 2, 8					
3 20 18	L FOB FCA	39 23 23	40 24 24	40	25	28	0 34 33	L FOB FCA					
4 40 35	1 6 6	40 24 24	41 25 25	41	26	29	2 27 28	0 15 13					
5 24 25	2 23 20	41 25 25	42 26 26	42	27	30	3 65 62	1 6 9					
6 20 20	4 22 20	42 26 26	43 27 27	43	28	31	4 24 26	2 41 36					
7 32 29	5 16 15	43 27 27	44 28 28	44	29	32	5 10 10	3 55 49					
8 28 28	6 30 28	44 28 28	45 29 29	45	30	33	6 42 42	4 12 11					
9 1 4	8 15 15	45 29 29	46 30 30	46	31	34							
		46 30 30	47 31 31	47	32	35							

Table 6 (continued)

6 21 22	6 35 36	7 12 11	5 42 38	1 19 17	6 11 10
7 27 22	8 19 18	8 3 4	6 35 33	3 9 9	7 30 31
H,K= 2, 9	9 39 38	9 10 11	7 19 18	4 4 8	8 16 15
L FOB FCA	10 16 17	H,K= 3, 9	9 40 38	6 13 11	11 2 1
0 24 22	12 5 7	L FOB FCA	10 21 19	7 13 14	H,K= 5, 5
2 6 4	13 8 8	0 32 27	12 20 19	H,K= 4, 10	L FOB FCA
3 11 10	H,K= 3, 4	1 11 9	13 7 11	L FOB FCA	1 22 21
4 9 9	L FOB FCA	2 14 12	H,K= 4, 4	0 26 23	3 11 11
6 20 20	0 11 11	3 14 16	L FOB FCA	1 6 8	4 3 6
7 11 10	1 88 90	4 2 3	0 22 24	2 7 8	5 12 10
8 2 4	2 21 21	6 26 23	1 54 57	3 2 1	6 18 17
H,K= 2, 10	3 12 12	7 15 13	2 57 56	4 21 16	7 26 24
L FOB FCA	4 48 46	H,K= 3, 10	3 46 49	H,K= 5, 0	8 4 8
0 25 22	5 23 25	L FOB FCA	4 24 22	L FOB FCA	9 20 20
2 20 18	7 2 6	0 7 12	5 33 30	0 10 9	10 2 9
3 7 7	8 18 19	1 2 1	6 17 17	2 72 74	11 20 18
4 11 10	9 4 9	2 10 10	7 13 11	4 9 9	H,K= 5, 6
H,K= 2, 11	10 32 30	3 3 5	8 31 30	6 58 53	L FOB FCA
L FOB FCA	11 2 6	4 24 23	9 2 5	8 14 12	0 21 20
0 12 10	H,K= 3, 5	5 3 2	H,K= 4, 5	10 21 21	1 19 17
1 3 4	L FOB FCA	H,K= 3, 11	L FOB FCA	12 17 20	2 20 19
H,K= 3, 0	0 35 34	L FOB FCA	0 18 20	H,K= 5, 1	3 28 25
L FOB FCA	1 12 13	0 20 19	1 34 30	L FOB FCA	4 10 11
0 28 32	2 16 15	H,K= 4, 0	2 16 18	0 49 53	5 19 18
2 51 58	3 2 4	L FOB FCA	3 21 21	1 7 8	6 24 24
4 65 64	4 39 35	0 29 29	4 7 9	2 2 4	7 19 17
6 56 57	5 34 33	2 76 88	5 21 19	3 22 22	8 2 2
8 29 26	6 17 18	4 13 13	6 10 11	4 13 13	9 6 11
10 15 15	7 29 27	6 53 55	7 21 20	5 26 28	10 8 12
12 36 37	8 2 5	8 2 3	9 22 21	6 30 28	H,K= 5, 7
H,K= 3, 1	9 17 16	10 29 28	10 2 7	7 19 20	L FOB FCA
L FOB FCA	10 2 5	12 15 15	12 8 9	8 15 12	0 29 28
0 18 15	11 14 14	H,K= 4, 1	H,K= 4, 6	9 11 12	1 34 29
2 50 49	12 7 11	L FOB FCA	L FOB FCA	10 26 26	2 8 7
3 17 17	H,K= 3, 6	0 5 7	0 18 17	11 5 10	4 10 10
4 35 40	L FOB FCA	1 16 19	2 35 34	H,K= 5, 2	5 13 13
5 25 26	0 17 16	2 23 27	3 46 42	L FOB FCA	6 4 11
6 2 3	1 12 14	3 7 8	4 19 18	0 22 23	7 20 19
7 10 11	2 11 11	4 33 32	5 21 19	1 39 40	H,K= 5, 8
8 37 39	3 47 49	5 23 22	6 19 19	2 26 26	L FOB FCA
9 25 24	4 7 6	6 19 19	7 23 22	3 9 9	0 4 7
13 7 8	5 5 8	7 22 22	8 12 11	4 29 27	1 13 12
H,K= 3, 2	6 8 6	8 31 32	10 2 6	5 3 2	2 3 5
L FOB FCA	7 16 15	9 19 17	H,K= 4, 7	6 29 27	3 12 13
0 78 87	8 14 12	10 26 23	L FOB FCA	7 19 20	4 23 23
1 75 77	9 20 19	11 3 9	0 2 6	9 10 10	5 20 17
2 107 119	10 13 13	12 9 10	1 29 27	11 19 19	7 3 8
3 3 6	H,K= 3, 7	13 8 10	3 20 17	H,K= 5, 3	H,K= 5, 9
4 79 74	L FOB FCA	H,K= 4, 2	4 5 11	L FOB FCA	L FOB FCA
5 57 58	1 21 20	L FOB FCA	5 17 17	0 44 45	0 26 25
6 35 34	3 10 9	0 21 23	6 8 6	1 12 12	1 9 10
7 22 20	4 25 23	1 4 5	7 19 19	2 17 21	2 5 6
8 36 33	5 8 10	2 68 70	9 5 12	3 55 53	5 8 10
9 6 8	6 22 18	3 28 26	10 9 10	5 15 17	H,K= 5, 10
10 3 3	7 30 26	5 13 13	H,K= 4, 8	7 2 3	L FOB FCA
11 24 25	8 8 11	6 34 35	L FOB FCA	8 2 8	0 15 13
12 22 21	11 16 16	7 15 13	0 31 29	9 16 16	1 8 9
13 5 8	H,K= 3, 8	8 1 5	1 7 7	11 17 13	H,K= 6, 0
14 3 5	L FOB FCA	9 3 4	2 14 12	H,K= 5, 4	L FOB FCA
H,K= 3, 3	0 2 4	13 13 11	3 21 20	L FOB FCA	0 15 18
L FOB FCA	1 8 9	H,K= 4, 3	4 13 12	0 49 50	2 77 73
0 40 44	2 19 18	L FOB FCA	5 12 11	1 38 39	4 9 11
1 17 18	3 30 26	0 1 4	7 3 5	2 3 4	6 31 33
2 24 24	4 11 11	1 24 24	H,K= 4, 9	3 69 68	8 4 4
3 51 46	5 6 10	2 2 5	L FOB FCA	4 25 23	10 7 8
5 82 81	6 10 9	3 35 39	0 7 8	5 27 26	

Table 6 (continued)

H,K= 6, 1	4 2 3	0 15 13	0 4 5	H,K= 9, 4	-7 29 28
L FOB FCA	5 23 22	2 12 12	1 30 27	L FOB FCA	-8 7 5
0 32 33	7 2 7	3 20 15	2 26 24	0 15 14	-9 20 20
1 2 3	8 4 5	4 11 11	4 4 7	1 2 6	-10 28 27
2 12 13	9 2 5	6 4 6	5 13 11	3 15 14	-11 36 34
3 8 10	H,K= 6, 7	7 19 19	6 5 10	5 3 8	-15 4 5
4 34 32	L FOB FCA	8 7 8	7 12 13	H,K= 9, 5	H,K= 0, 3
5 20 18	0 2 4	9 5 7	8 2 3	L FOB FCA	L FOB FCA
6 30 30	1 32 28	H,K= 7, 5	H,K= 8, 4	1 14 13	-1 8 8
9 16 15	3 11 12	L FOB FCA	L FOB FCA	2 4 5	-2 23 23
10 23 23	4 2 3	0 30 30	0 2 5	3 3 6	-3 86 98
H,K= 6, 2	6 13 13	1 29 25	1 4 5	H,K= 9, 6	-4 3 2
L FOB FCA	7 17 17	2 18 15	2 9 8	L FOB FCA	-6 10 12
1 11 11	H,K= 6, 8	3 9 10	3 15 13	0 7 11	-7 83 80
2 31 29	L FOB FCA	4 25 25	5 23 20	1 6 9	-8 8 8
3 54 51	0 13 13	5 20 20	7 10 10	H,K= 10, 0	-9 1 4
4 48 46	1 12 14	6 6 7	H,K= 8, 5	L FOB FCA	-10 5 4
5 3 5	4 15 13	7 2 3	L FOB FCA	0 3 4	-11 26 22
6 20 17	5 22 18	8 10 10	1 27 25	2 8 7	-12 7 7
7 21 22	H,K= 6, 9	H,K= 7, 6	2 11 9	4 7 8	-13 13 10
8 13 13	L FOB FCA	L FOB FCA	3 15 14	H,K= 10, 1	-14 7 7
9 12 12	0 3 5	1 26 27	5 6 7	L FOB FCA	H,K= 0, 4
11 2 7	1 3 8	2 8 8	6 8 10	0 5 6	L FOB FCA
H,K= 6, 3	2 3 5	3 23 22	H,K= 8, 6	1 12 12	-1 61 62
L FOB FCA	H,K= 7, 0	4 17 17	L FOB FCA	2 14 12	-2 84 86
0 33 35	L FOB FCA	5 19 17	2 13 14	H,K= 10, 3	-3 19 18
1 17 17	0 9 13	H,K= 7, 7	4 5 7	L FOB FCA	-4 34 35
2 34 31	2 19 17	L FOB FCA	5 29 27	1 16 12	-5 25 25
3 19 18	4 12 10	0 15 15	H,K= 8, 7	2 2 4	-6 20 20
4 13 12	6 18 17	1 20 18	L FOB FCA	H,K= 10, 4	-7 33 29
5 23 24	8 21 18	2 2 4	0 6 9	L FOB FCA	-8 27 28
8 19 20	H,K= 7, 1	3 11 10	1 7 9	0 6 5	-9 5 4
9 18 18	L FOB FCA	6 2 5	3 14 12	H,K= 0, 0	-11 37 35
10 2 7	0 55 53	H,K= 7, 8	H,K= 9, 0	L FOB FCA	-12 11 8
H,K= 6, 4	1 11 11	L FOB FCA	L FOB FCA	-2 53 52	-13 9 9
L FOB FCA	2 11 10	0 13 12	0 5 4	-4 71 78	-14 7 8
0 23 22	3 1 5	1 17 17	2 4 5	-6 46 46	H,K= 0, 5
1 23 24	4 8 8	3 2 2	4 23 22	-8 25 23	L FOB FCA
2 15 15	5 6 7	H,K= 8, 0	6 12 11	-10 32 31	-1 39 37
3 32 31	6 16 15	L FOB FCA	H,K= 9, 1	-12 7 7	-2 17 17
4 38 36	7 12 12	0 7 8	L FOB FCA	-14 28 28	-3 46 44
5 13 14	10 14 13	2 8 10	0 34 29	H,K= 0, 1	-4 16 17
6 14 14	H,K= 7, 2	4 58 55	1 22 19	L FOB FCA	-5 24 28
7 34 32	L FOB FCA	6 12 10	2 14 11	-1 15 19	-6 18 13
8 11 11	1 3 4	8 15 15	H,K= 9, 3	-2 39 43	-7 33 33
H,K= 6, 5	3 39 41	H,K= 8, 1	L FOB FCA	-3 62 65	-8 4 7
L FOB FCA	4 9 9	L FOB FCA	3 2 3	-4 82 79	-9 15 13
0 15 15	5 2 5	0 33 31	H,K= 9, 1	-5 57 52	-10 25 22
1 22 21	6 14 13	1 7 8	L FOB FCA	-6 32 30	-12 31 27
2 27 25	7 22 22	2 24 22	5 5 6	-7 51 47	H,K= 0, 6
4 18 19	8 21 22	4 41 36	6 3 3	-8 28 26	L FOB FCA
6 14 12	9 3 6	5 4 5	H,K= 9, 2	-9 15 16	-1 51 49
7 17 16	10 12 12	6 5 7	L FOB FCA	-10 3 4	-2 64 54
8 2 7	H,K= 7, 3	7 6 7	0 3 6	-11 13 15	-3 40 37
9 3 6	L FOB FCA	8 6 5	1 3 3	-12 3 5	-4 23 22
H,K= 6, 6	0 8 9	H,K= 8, 2	3 15 12	-13 3 3	-5 5 6
L FOB FCA	1 21 20	L FOB FCA	4 8 7	-14 40 39	-6 15 19
1 17 17	2 2 5	1 17 16	6 5 7	-15 10 9	-7 1 2
2 19 19	3 2 4	2 6 7	H,K= 9, 3	H,K= 0, 2	-8 14 11
3 4 7	4 2 5	3 19 17	L FOB FCA	L FOB FCA	-9 7 7
	6 2 4	4 17 15	0 5 6	-1 6 6	-11 7 9
	7 8 7	6 10 10	1 23 20	-2 57 64	-13 26 24
	8 13 12	7 19 16	2 20 16	-3 27 25	H,K= 0, 7
	9 4 8	8 10 10	5 14 15	-4 37 39	L FOB FCA
H,K= 7, 4	L FOB FCA	H,K= 8, 3	6 6 5	-5 15 16	-1 61 53
		L FOB FCA		-6 7 7	-2 2 5

Table 6 (continued)

-3 13 11	-1 13 14	-7 26 25	-6 68 70	-13 2 6	H,K= 3, 1
-4 29 29	-2 8 10	-8 21 18	-7 10 10	H,K= 2, 6	L FOB FCA
-5 47 43	-3 61 65	-9 16 15	-8 9 6	L FOB FCA	-1 17 15
-6 4 8	-4 58 63	-10 30 27	-9 20 17	-1 50 49	-2 125 147
-8 7 8	-5 2 2	-11 13 11	-10 45 40	-3 17 13	-3 17 19
-9 26 25	-6 22 21	-12 4 7	-11 4 4	-4 19 16	-5 29 30
-10 12 13	-7 6 7	-13 12 12	-12 3 6	-6 12 15	-6 86 87
H,K= 0, 8	-8 12 10	H,K= 1, 7	-13 25 23	-7 19 19	-7 23 21
L FOB FCA	-9 21 19	L FOB FCA	H,K= 2, 2	-8 14 15	-8 28 26
-1 10 12	-10 26 23	-1 35 31	L FOB FCA	-9 3 9	-10 9 10
-2 24 22	-12 11 8	-2 16 13	-1 39 45	-10 2 4	-12 21 19
-3 16 16	-13 2 2	-3 11 9	-2 15 16	-11 22 20	-13 10 10
-4 2 4	-14 6 6	-4 12 9	-3 54 61	-12 7 9	-14 4 7
-5 4 6	-15 5 9	-5 65 60	-5 48 46	H,K= 2, 7	H,K= 3, 2
-7 4 8	H,K= 1, 3	-6 12 13	-6 41 38	L FOB FCA	L FOB FCA
-8 10 15	L FOB FCA	-7 2 2	-7 2 2	-1 39 33	-1 47 50
-9 5 11	-1 59 59	-8 10 12	-8 48 46	-2 37 35	-2 53 52
-10 5 6	-2 37 40	-9 36 36	-9 18 17	-3 14 12	-3 40 44
-11 3 3	-3 78 86	-10 2 5	-10 30 29	-4 2 6	-4 32 33
H,K= 0, 9	-4 24 29	H,K= 1, 8	-11 9 11	-5 30 33	-5 52 54
L FOB FCA	-5 18 18	L FOB FCA	-12 5 6	-6 18 18	-6 18 19
-1 5 6	-6 28 28	-1 42 39	-13 21 19	-9 14 13	-7 20 20
-2 22 20	-7 83 79	-2 33 31	-14 6 8	-11 17 16	-8 1 2
-4 22 20	-8 22 22	-3 4 3	H,K= 2, 3	H,K= 2, 8	-9 69 62
-5 15 15	-9 9 8	-5 11 10	L FOB FCA	L FOB FCA	-10 4 7
-6 30 28	-10 6 5	-7 3 2	-1 39 41	-1 47 45	-11 7 8
-8 16 15	-11 25 22	-8 4 10	-3 43 47	-2 9 7	-13 21 18
-9 12 13	-12 3 5	-9 14 15	-4 51 59	-3 14 13	-14 10 9
H,K= 0, 10	-13 16 13	-10 3 5	-5 17 17	-4 4 6	-15 3 4
L FOB FCA	-14 3 6	H,K= 1, 9	-6 9 7	-6 2 7	H,K= 3, 3
-2 39 34	H,K= 1, 4	L FOB FCA	-7 29 28	-7 17 15	L FOB FCA
-4 2 2	L FOB FCA	-1 17 16	-8 22 20	-9 2 6	-1 3 8
-5 9 7	-1 40 40	-2 15 15	-9 33 30	-11 9 11	-2 3 5
-6 8 9	-2 39 35	-3 2 3	-10 20 19	H,K= 2, 9	-3 30 32
H,K= 0, 11	-3 56 58	-4 18 15	-11 21 22	L FOB FCA	-4 61 66
L FOB FCA	-4 31 30	-5 30 29	-12 4 7	-1 16 13	-5 14 14
-1 3 5	-6 31 32	-6 18 17	-13 16 15	-3 2 5	-6 13 14
-2 4 4	-7 13 13	-8 13 12	-14 12 11	-4 34 31	-7 35 34
-3 6 5	-8 21 19	H,K= 1, 10	-15 4 6	-8 2 7	-8 4 7
-4 10 11	-9 31 30	L FOB FCA	H,K= 2, 4	H,K= 2, 10	-9 17 17
H,K= 1, 0	-10 31 29	-1 4 5	L FOB FCA	L FOB FCA	-10 19 20
L FOB FCA	-11 2 4	-2 40 32	-1 6 6	-1 2 3	-12 5 7
-2 49 48	-12 19 17	-4 9 10	-2 37 39	-2 12 10	-13 17 17
-4 55 60	-13 4 8	-5 8 5	-3 56 61	-3 2 1	H,K= 3, 4
-6 42 43	H,K= 1, 5	-6 8 8	-4 5 8	-4 14 14	L FOB FCA
-8 65 63	L FOB FCA	H,K= 1, 11	-5 38 40	-5 5 7	-1 19 17
-10 71 66	-1 17 16	L FOB FCA	-6 35 32	H,K= 2, 11	-2 20 19
-12 8 6	-2 6 4	-1 5 5	-7 10 9	L FOB FCA	-3 17 21
-14 40 37	-3 30 28	-3 16 15	-8 26 25	-1 4 8	-4 19 17
H,K= 1, 1	-4 31 33	-4 9 9	-9 8 6	-2 5 7	-5 5 8
L FOB FCA	-5 46 47	H,K= 2, 0	-11 11 11	-3 4 6	-6 11 12
-1 35 35	-6 13 13	L FOB FCA	-12 26 26	-4 23 22	-7 21 22
-2 33 35	-7 33 31	-2 3 4	-13 14 12	H,K= 3, 0	-9 42 39
-3 113 118	-8 2 3	-4 36 35	-14 3 5	L FOB FCA	-11 2 7
-4 48 47	-9 20 18	-6 50 48	H,K= 2, 5	-2 81 86	-12 11 11
-5 56 51	-10 5 6	-8 6 7	L FOB FCA	-4 2 2	-13 22 19
-6 66 62	-12 3 3	-10 65 58	-1 45 48	-6 8 10	-14 13 12
-7 53 51	-13 5 8	-12 2 1	-2 6 9	-8 14 15	H,K= 3, 5
-8 29 29	-14 6 7	-14 11 11	-3 35 35	-10 16 14	L FOB FCA
-9 3 5	H,K= 1, 6	H,K= 2, 1	-4 7 8	-14 2 2	-1 38 41
-11 3 6	L FOB FCA	L FOB FCA	-5 18 19		-2 37 38
-12 5 7	-1 49 44	-1 43 49	-6 37 37		-3 41 43
-13 8 9	-3 18 16	-2 78 89	-8 36 33		-4 35 40
-14 2 4	-4 35 34	-3 51 54	-10 16 15		-5 45 46
H,K= 1, 2	-5 37 37	-4 9 10	-11 3 5		-6 31 31
L FOB FCA	-6 11 11	-5 16 16	-12 19 16		-7 24 23
					-8 21 21

Table 6 (continued)

-9 14 15	-10 30 29	-7 18 17	-9 6 6	-2 12 13	-8 4 6
-10 22 19	-12 29 27	-10 3 7	-10 14 15	-5 4 7	-9 26 25
-13 8 9	-13 6 9	-11 23 22	-11 17 16	H,K= 5, 9	-10 3 5
H,K= 3, 6	-14 4 6	H,K= 4, 7	-12 22 19	L FOB FCA	-11 13 13
L FOB FCA	H,K= 4, 2	L FOB FCA	-13 15 14	-2 19 16	-12 2 5
-1 41 39	L FOB FCA	-1 14 14	H,K= 5, 3	-3 9 11	H,K= 6, 5
-2 18 18	-1 18 22	-2 2 3	L FOB FCA	-4 11 12	L FOB FCA
-3 18 14	-3 47 49	-3 28 26	-1 79 84	H,K= 5, 10	-1 24 23
-6 5 10	-4 3 5	-4 19 18	-2 25 26	L FOB FCA	-2 9 11
-7 26 25	-5 45 44	-6 8 11	-3 7 9	-2 8 9	-3 26 26
-9 9 12	-6 4 6	-7 17 18	-4 20 22	H,K= 6, 0	-4 8 9
-10 15 15	-7 26 25	-9 11 13	-5 33 33	L FOB FCA	-5 24 23
-11 11 12	-8 24 24	-10 2 7	-6 4 7	-2 8 10	-7 15 13
H,K= 3, 7	-9 36 32	H,K= 4, 8	-7 24 23	-4 38 37	-8 6 7
L FOB FCA	-10 17 15	L FOB FCA	-8 4 7	-6 12 11	H,K= 6, 6
-1 12 15	-11 14 13	-1 15 13	-9 12 11	-8 41 36	L FOB FCA
-2 26 27	-12 24 22	-2 10 10	-11 16 13	-10 31 33	-1 3 5
-3 27 25	-13 7 7	-3 12 14	-13 2 4	-12 12 8	-2 16 15
-5 34 33	-14 13 11	-4 10 9	-14 11 12	H,K= 6, 1	-3 9 12
-6 16 19	H,K= 4, 3	-5 5 9	H,K= 5, 4	L FOB FCA	-4 26 25
-7 4 7	L FOB FCA	-6 5 10	L FOB FCA	-1 17 16	-5 19 20
-9 2 5	-1 57 65	-7 8 14	-2 17 19	-2 30 32	-6 2 4
H,K= 3, 8	-2 17 18	-8 14 16	-3 19 19	-3 17 18	-7 21 21
L FOB FCA	-3 19 18	H,K= 4, 9	-4 2 3	-4 50 47	-8 22 23
-1 32 30	-4 24 26	L FOB FCA	-5 20 19	-5 29 28	-9 2 6
-2 10 10	-5 67 65	-1 3 6	-6 33 35	-7 17 14	H,K= 6, 7
-3 17 17	-7 8 9	-2 6 8	-7 16 15	-8 11 11	L FOB FCA
-5 2 9	-8 32 30	-3 20 17	-8 12 12	-9 7 10	-1 15 15
-7 31 33	-9 13 11	-4 32 29	-9 14 12	-10 18 16	-3 35 35
-8 20 21	-11 15 14	-6 2 1	-10 11 9	-11 21 19	-4 18 18
-9 3 6	-12 20 17	-7 12 16	-12 5 8	-12 2 6	-6 4 10
-10 16 18	-13 5 6	H,K= 4, 10	-13 11 11	H,K= 6, 2	-7 16 16
H,K= 3, 9	-14 2 5	L FOB FCA	H,K= 5, 5	L FOB FCA	-9 19 17
L FOB FCA	H,K= 4, 4	-4 3 7	L FOB FCA	-1 31 33	H,K= 6, 8
-1 4 7	L FOB FCA	-6 15 13	-1 22 24	-2 10 10	L FOB FCA
-2 2 4	-1 26 28	H,K= 5, 0	-3 21 22	-3 16 15	-1 6 7
-3 21 21	-2 36 36	L FOB FCA	-4 19 20	-4 18 18	-2 2 2
-4 31 28	-3 23 26	-2 48 50	-5 6 11	-5 11 12	-4 4 9
-5 5 8	-4 12 13	-4 83 81	-6 14 14	-6 18 17	-5 9 12
-8 8 15	-5 34 35	-6 16 15	-8 2 6	-7 12 10	-6 8 12
-9 4 9	-6 9 13	-8 50 47	-10 2 9	-8 23 19	-7 2 8
H,K= 3, 10	-7 2 6	-10 2 3	-11 3 6	-9 19 19	H,K= 6, 9
L FOB FCA	-8 18 18	-12 19 15	H,K= 5, 6	-11 7 7	L FOB FCA
-1 2 2	-9 26 25	-14 8 8	L FOB FCA	-12 4 10	-3 2 8
-3 5 8	-10 4 9	H,K= 5, 1	-1 24 22	H,K= 6, 3	H,K= 7, 0
-6 2 4	-11 5 8	L FOB FCA	-2 4 7	L FOB FCA	L FOB FCA
H,K= 3, 11	-12 3 7	-1 26 28	-3 19 19	-1 41 40	-2 5 7
L FOB FCA	-13 2 6	-2 53 57	-4 17 17	-2 19 19	-4 13 11
-1 3 5	H,K= 4, 5	-3 31 31	-5 3 8	-3 12 13	-6 4 6
-2 11 10	L FOB FCA	-4 20 21	-6 11 13	-4 26 24	-8 22 18
H,K= 4, 0	-1 51 51	-5 18 20	-7 31 32	-5 41 40	-10 18 15
L FOB FCA	-2 19 20	-6 34 35	-8 20 18	-6 14 13	-12 32 29
-2 39 44	-3 36 39	-7 23 20	-10 5 8	-7 9 11	H,K= 7, 1
-4 39 39	-4 26 28	-8 12 12	-11 7 6	-10 14 16	L FOB FCA
-6 28 23	-5 43 45	-9 16 16	-12 3 7	-11 22 20	-1 19 19
-8 58 51	-6 9 11	-12 11 11	H,K= 5, 7	-12 17 16	-2 2 4
-10 20 22	-7 14 15	H,K= 5, 2	L FOB FCA	-13 2 3	-4 21 20
-12 3 4	-8 17 16	L FOB FCA	-1 15 14	H,K= 6, 4	-5 2 4
H,K= 4, 1	-10 12 11	-1 11 12	-3 35 34	L FOB FCA	-6 19 17
L FOB FCA	-12 7 11	-2 28 29	-4 16 15	-1 18 18	-7 3 2
-1 18 19	H,K= 4, 6	-3 20 20	-5 12 17	-2 39 38	-11 11 10
-2 36 39	L FOB FCA	-4 16 18	-9 2 6	-3 11 12	H,K= 7, 2
-3 9 8	-1 40 38	-5 1 2	H,K= 5, 8	-4 15 13	L FOB FCA
-4 13 15	-2 37 37	-6 7 8	L FOB FCA	-6 23 20	-1 15 14
-5 24 25	-4 8 12	-7 7 8	-1 10 10	-7 21 20	-2 3 6
-6 35 36	-6 2 3	-8 27 25			-3 29 26
-8 13 10					

Table 6 (continued)

-4 25 23	-2 12 12	-5 2 3	-2 15 13	-4 9 8	-4 4 4
-5 1 5	-3 27 23	-8 4 6	-3 15 14	-7 11 10	H,K= 10, 0
-6 22 19	-4 21 20	-10 27 26	-4 7 8	H,K= 9, 3	L FOB FCA
-7 25 23	-6 7 10	H,K= 8, 2	-5 3 4	L FOB FCA	-2 23 17
-8 14 14	-10 7 9	L FOB FCA	-6 19 19	-2 7 9	-4 2 1
-9 3 8	H,K= 7, 6	-1 14 13	-8 5 12	-3 23 19	-6 23 20
-10 19 16	L FOB FCA	-2 25 21	-9 22 20	-5 4 10	H,K= 10, 1
-11 10 10	-1 24 23	-3 25 20	H,K= 8, 6	-8 3 6	L FOB FCA
-12 7 8	-2 6 9	-4 12 11	L FOB FCA	H,K= 9, 4	-2 2 2
H,K= 7, 3	-5 18 17	-5 18 15	-1 17 16	L FOB FCA	-3 2 4
L FOB FCA	H,K= 7, 7	-6 23 21	-2 3 7	-1 18 16	H,K= 10, 2
-1 27 27	L FOB FCA	-7 19 15	-4 3 8	-2 5 6	L FOB FCA
-2 22 20	-1 20 17	-8 12 13	-5 6 8	-3 15 14	-2 8 8
-3 4 7	-3 21 20	-10 13 15	H,K= 9, 0	-5 22 20	-3 9 8
-5 25 23	-4 12 11	-11 8 7	L FOB FCA	-6 3 9	-4 5 6
-7 8 12	-7 6 8	H,K= 8, 3	-2 21 19	-7 9 9	-5 2 4
-9 10 12	H,K= 7, 8	L FOB FCA	-4 13 13	H,K= 9, 5	-6 19 15
-10 2 5	L FOB FCA	-1 13 13	-6 22 16	L FOB FCA	-7 8 10
-11 2 7	-2 2 5	-2 25 21	-10 12 12	-1 20 17	H,K= 10, 3
H,K= 7, 4	-5 8 11	-3 9 8	H,K= 9, 1	-2 5 7	L FOB FCA
L FOB FCA	-6 2 6	-4 4 7	L FOB FCA	-3 16 13	-3 9 9
-1 20 19	H,K= 8, 0	-5 4 9	-2 17 15	-4 7 9	-4 8 8
-2 12 11	L FOB FCA	-9 8 8	-3 5 6	-6 8 9	-5 11 10
-3 28 26	-2 6 6	H,K= 8, 4	-4 20 16	H,K= 9, 6	H,K= 10, 4
-4 2 6	-4 18 16	L FOB FCA	-6 12 12	L FOB FCA	L FOB FCA
-6 15 14	-6 31 25	-1 6 7	-7 2 1	-1 4 4	-1 15 12
-7 27 26	-8 19 17	-3 30 25	-10 5 7	-3 5 10	-2 9 9
-8 3 7	H,K= 8, 1	-4 2 2	H,K= 9, 2		-4 9 11
-10 28 24	L FOB FCA	-5 11 10	L FOB FCA		
-11 5 5	-1 8 9	-6 11 11	-1 7 7		
H,K= 7, 5	-2 8 8	-7 19 17	-2 23 22		
L FOB FCA	-3 11 11	H,K= 8, 5	-3 7 8		
-1 17 16	-4 30 26	L FOB FCA			
		-1 4 7			

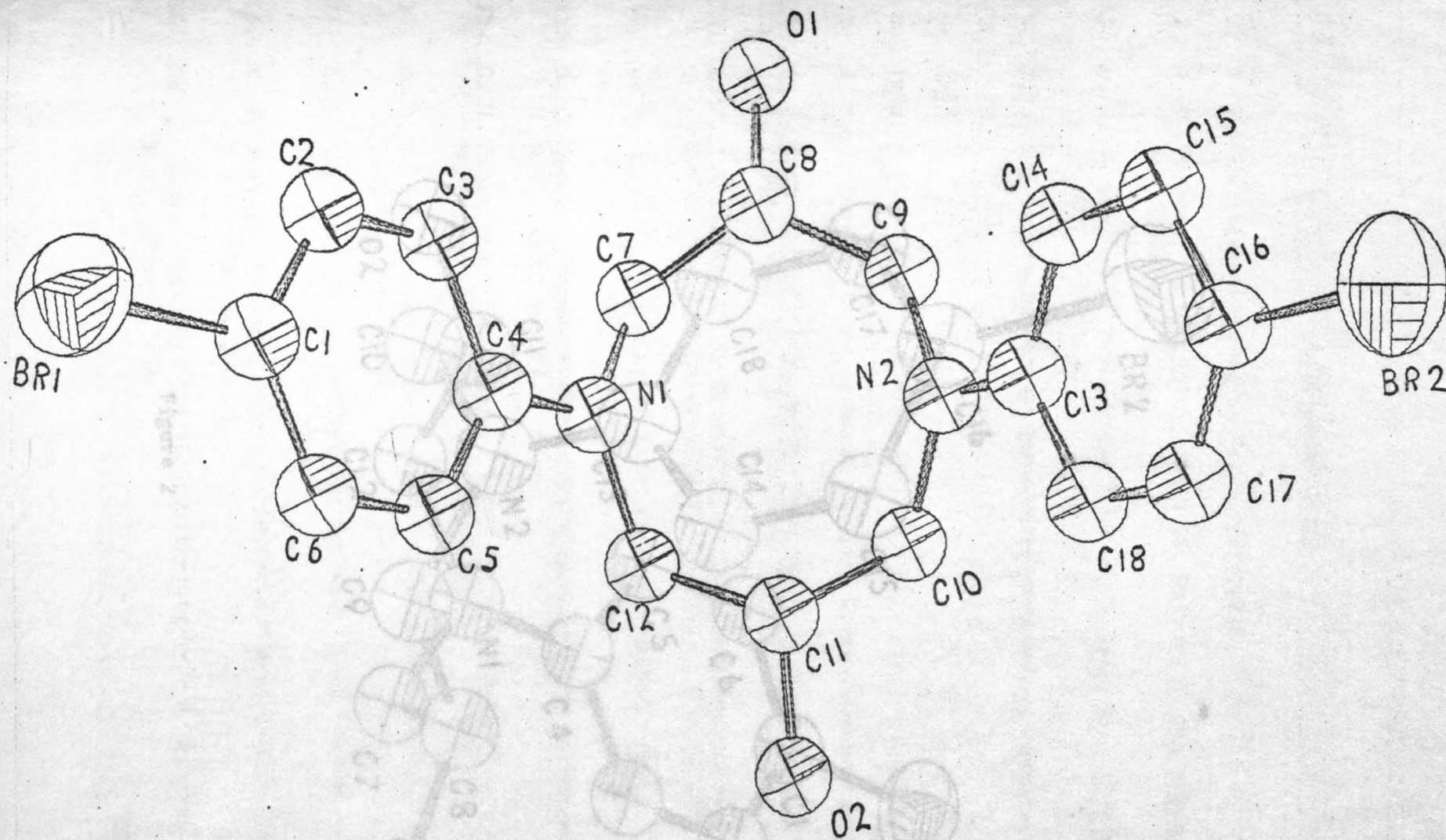


Figure 1.

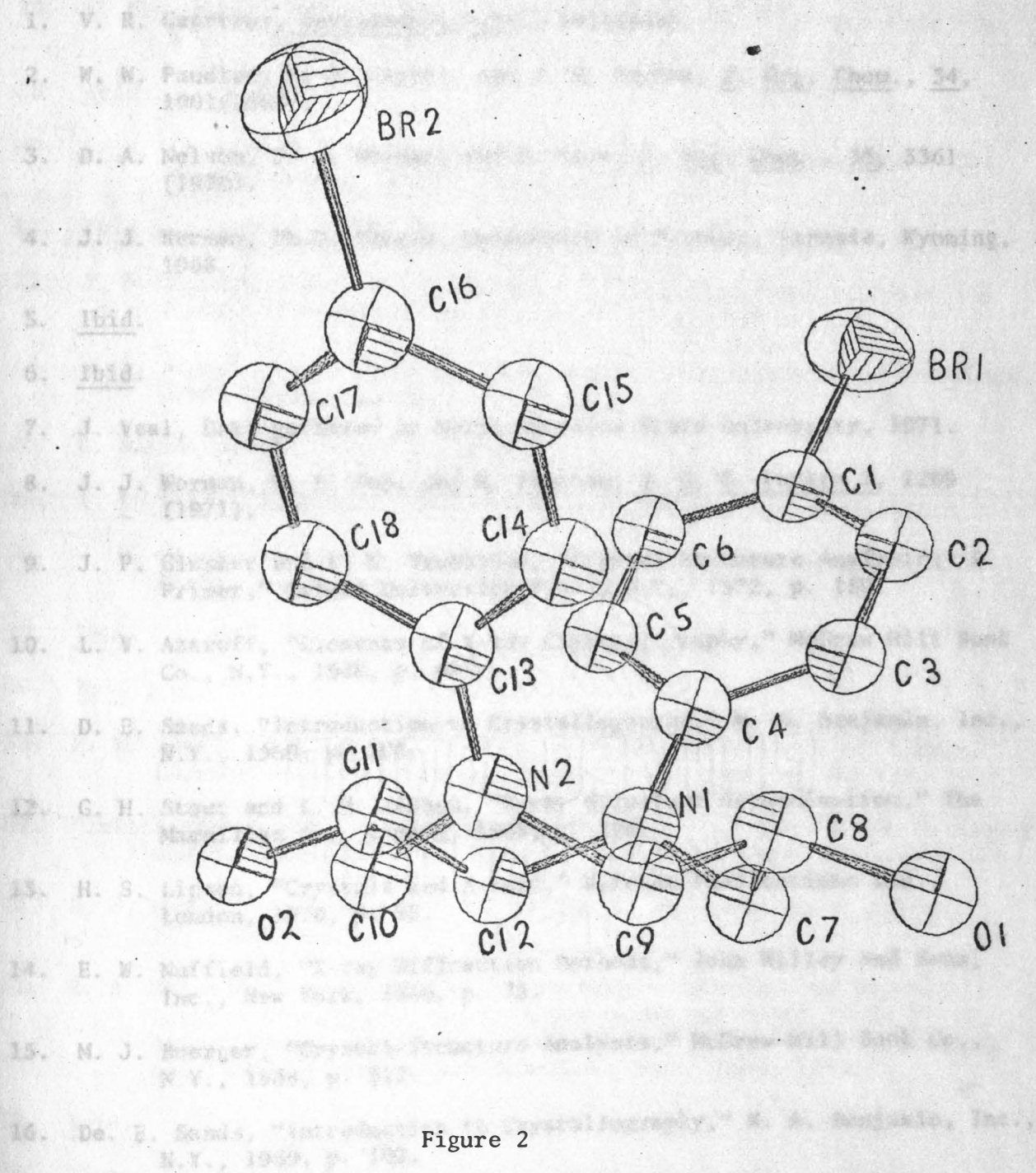


Figure 2

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